SYMPOSIUM V
Thin Films–Stresses and Mechanical Properties VIII
November 29 – December 3, 1999

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Proceedings published as Volume 594
of the Materials Research Society
Symposium Proceedings Series.

*Invited paper
SESSION V1: MULTILAYERED FILMS
Chairs: Brian Joseph Daniels and Neville R. Moody Monday Afternoon, November 29, 1999
Room 306 (H)

1:30 PM V1.1
INTERFACE STRESS: MEASUREMENT AND EFFECTS ON THE STRESSES IN THIN FILMS. Franz Spieger, Division of Engineering and Applied Sciences, Harvard University, Cambridge MA.

Recent progress in the measurement of interface stresses is reviewed. There are now several methods of measuring the interface stress of epitaxial (111) Ag/Ni interfaces. They give consistent, strongly compressive, values. Theoretical arguments for this compressive sign, based on the non-linear elasticity of the interface dislocations, are given. The effect of interface roughness and perpendicular grain boundaries on the measurement of the interface stress is estimated. The result shows that roughness may account for the lower interface stress measured in multilayers with the smallest repeat lengths. The effect of the inter-plane stress on the early compressive stage in the stress evolution during deposition is discussed.

2:00 PM V1.2
DETERMINATION OF INTERFACE STRESS FROM TRANSMISSION X-RAY DIFFRACTION OF FREESTANDING ALUMINUM/TITANIUM MULTILAYERS. Daniel Josell and J.E. Bonevich, National Institute of Standards and Technology, Gaithersburg, MD; Ingrid X. Sioe and Robert C. Cammisa, Johns Hopkins University.

As individual layers in thin films become thinner, the stress associated with the presence of internal interfaces, and derivable from equilibrium thermodynamics, can become significantly larger than the deposition stress. The thermodynamic quantities that determine the magnitude of this stress is the interface stress. It equals the strain energy of a fixed number of atoms on an interface with respect to equal in-plane strains of the layers immediately adjacent to the interface. It thus represents the ability of the system to lower its free energy by reducing the free energy of the interface at the expense of added strain energy within the adjacent material. We have measured the interface stress of interfaces between (111) aluminum and (1001) titanium layers using transmission x-ray diffraction studies of free-standing titanium multilayers. The interface stress was determined from the dependence of the in-plane aluminum and titanium lattice constants on the thickness of the aluminum/titanium bilayers and the elemental stiffness tensors. Past measurements of interfacial stress studied multilayer thin films attached to substrates, and therefore required additional studies of substrate curvature, and the stiffness tensor of the substrate, to correct for forces applied by the substrate.

2:15 PM V1.3
DEFORMATION MECHANISM MAPS FOR POLYCRYSTALLINE METALLIC MULTILAYERS. M. Merz, M. Verder, H. Kung, J.D. Embury and J. Birth, Los Alamos National Lab, Materials Science and Technology Division, Los Alamos, NM.

Metallic multilayers provide the opportunity to synthesize materials close to the theoretical interface toughness and to understand the role of length scales in metal plasticity. Refinement of the microstructure from the micron-scale to the nanometer-scale may give rise to different deformation modes involving continuum pile-up (Hull-Petch), discrete pile-up (modified Hull-Petch) and single dislocation (Orowan). Diffusion-based mechanisms such as Coble creep may be operative causing softening below a critical microstructural-scale in the nanometer range. For polycrystalline metallic multilayers, we present a simple analysis that allows us to obtain limiting values of microstructural scales at which these different mechanisms operate. We present the results in the form of two-dimensional maps of layer thickness and composition. The maps show if different deformation mechanisms operate. These maps are intended to be guidelines for interpreting the scale-dependent strengthening or softening mechanisms in multilayers. Other factors, besides length scale, that may influence the transition from one mechanism to another are discussed. This research is sponsored by DOE-OBES.

2:30 PM V1.4
AN X-RAY INVESTIGATION OF RESIDUAL STRESSES AND BENDING STRESSES IN FREE-STANDING Nb/Nb3Si2, MCRLAMINATES. C. H. Shang, D. Van Heerden, A. J. Gavens, and T. P. Weihs, Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, MD.

Vapor deposited metal silicide microstructures are currently being developed to serve as thin (~300µm) outer walls in future, high-temperature superconducting designs. Controlling and limiting the thermal stress and bending stresses in these components will be critical to their performance. Here we present X-ray analyses of these structures in model microstructure systems that contain many micro thick layers of Nb and Nb3Si2. The samples were sputter deposited at room temperature, removed from their substrates, and then annealed at 1200 °C for 3 hours. The residual stresses and bending stresses in the individual layers were then quantified after cooling using non-symmetric X-ray diffraction. Large residual stresses (~300Mpa) were found in samples that were finally annealed and these stresses are attributed to a mismatch in the thermal expansion coefficients for the Nb and Nb3Si2 phases. The Nb layers were in tension and the silicide layers were in compression. However, even larger (~500Mpa) bending stresses were also detected in multilaminates that were cut after annealing and then flattened for the X-ray measurements. In these samples the Nb and Nb3Si2 layers were in compression due to the bending stresses that resulted from the flattening. By characterizing strains in the top Nb3Si2 layer, both normal and parallel to the bending axis, a Poisson's ratio of ε11=1.94 was determined for the poly-crystalline Nb3Si2 phase.

2:45 PM V1.5
ASPECTS OF PLASTICITY IN METALLIC MULTILAYERS. M. Merz, M. Verder, H. Kung, J.D. Embury, Harriet King, Los Alamos National Laboratory, Los Alamos, NM.

The properties of metallic multilayers is influenced by the scale, the epitaxy, the residual stresses and the interface mixing. In attempting to produce models of plastic deformation, one must consider factors such as difference in shear moduli, internal stress and detailed nature of interface. This includes a variety of systems can be used to control these factors such as Cu/Ni, Cu/Cr, Cu/Ag and Cu/Nb. In order to reduce the mechanical properties, dedicated experiments were designed: injection of dislocations from a single crystal substrate into the multilayer, penetration by a nanodotter, tensile tests on free standing films, and measurement of the residual stress. The results on both mechanical tests and detailed characterization of microstructure will be integrated within models describing the plasticity of multilayers. Special focus will be given concerning the effect of polycrystallinity of the layer on the mechanical properties, and construction of deformation mechanism maps. This research is sponsored by DOE-OBES.

3:30 PM V1.6
STRESS IN SPIN VALVE MULTILAYERS DURING ANITFERROMAGNETIC PHASE TRANSFORMATION. B.J. Daniels, S.P. Bozeman, and H. Hsu, Seagate Research Head, Minneapolis, MN.

The stresses in various samples of sputter-deposited, Ni/Mn-pinned spin valve multilayers were measured using a laser-based wafer curvature technique. Average as-deposited stresses of up to 1 GPa were measured. The average stress was a strong function of the composition of the multilayer stack as well as properties of the amorphous oxide underlayer. These films were then subjected to an anneal field at 4°C for 2 hours at 300°C. This anneal causes the antiferromagnetic layer, Ni/Mn, to undergo a phase transformation from the face-centered cubic (fcc) to the face-centered tetragonal (fct) crystal structure. This phase transformation induces the average stress in some of the films to approximately 1.5 GPa. Stress changes during the antiferromagnetic phase transformation were also observed as a function of annealing temperature and time during substrate heating, annealing, and cooling. The stresses varied linearly with temperature during the heating and cooling of the substrate, indicating that the bulk of the phase transformation occurs during the isothermal portion of the anneal. By monitoring stress vs. time during the isothermal anneal, the extent of the antiferromagnetic phase transformation was determined. Final stress data obtained from the wafers annealed in the wafer curvature system (no applied magnetic field) are in good agreement with those obtained using a conventional magnetic annealing system. Analysis of data for PdMn-based spin valve multilayers is still in progress.

3:45 PM V1.7

TiN/NiN multilayers, with bulkier thickness between 10 nm and 50 nm and a total film thickness of 1-3 µm, have been grown by UHV reactive magnetron sputtering deposition into MgO (-0.5%) and (111) substrates held at temperatures ranging from 660 °C to 800 °C. The hardness has been measured by nanoindentation, and the nanodeformed and deformed structures have been observed in cross section by transmission electron microscopy. Here we report on TEM observations of the nanodeformation microstructure and the nanoindentation results of TiN/NiN multilayers grown under different conditions.
...deposited films showed that whilst optical growth of the multilayers occurred in the first few layers, this soon breaks down giving rise to the formation of a columnar structure, which is inclined to the substrate surface. It is shown that the extent of this transition depends on the bilayer thickness and the orientation of the substrate. The measured hardness of the films was similar to that of the softer component TiN or TiN, and SEM observations of the deformed structures showed that cracking and shearing between the layers had occurred. It is possible that the measured hardness was limited by the loss of epitaxy, and experiments have been carried out to optimise the deposition conditions in order to obtain epitaxial layers through the whole thickness of the multilayers.

4:00 P.M. V1.8
INFLUENCE OF NANO-METER-SCALE MULTILAYERED THIN FILM COATING ON FATIGUE CRACK INITIATION. M. Stoudt and R.F. Ridley, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD; B.C. Chien, Johns Hopkins University, Department of Materials Science and Engineering, Baltimore, MD.

Multilayered Cu-Ni thin films were electrodeposited onto amorphous polycrystalline copper cylindrical substrates. The bilayer repeat length of the multilayered coatings was 2nm, and the overall thickness of the coatings was 5nm. These samples were investigated in bending fatigue with a stress amplitude about 50% higher than the yield stress, and found to have a lifetime-to-failure of at least an order of magnitude greater than that of the bare copper substrates and that of substrates with 5nm thick electrodeposited coatings of Cu or Ni. These results will be discussed in relation to mechanisms of fatigue crack initiation and the influence of the intrinsic stress and the nanoscale layer thickness of the electrodeposited multilayered films. In particular, the role of the multilayered films in suppressing dislocation multiplication and multiplication leading to enhanced fatigue lifetime will be presented.

4:15 P.M. V1.9
PROCESSES, MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF Ni/NiAl MULTILAYERED THIN FILMS. Rajeshri Barcadera, Jason Fair, Peter M. Anderson, Hamish L. Fraser, The Ohio State University, Dept. of Materials Science and Engineering, Columbus, OH.

The NiNiAl system is the basis of a large number of Nb-based superalloys used extensively in the aerospace industry. The mechanical properties of bulk superalloys, which primarily consist of a Ni-based matrix reinforced with cubical precipitates of NiAl, have been extensively researched. The goal of the present study is to investigate the mechanical properties of multilayered Ni/ NiAl nano-composites in the thin film form. These multilayers have been processed using UHV magnetron sputtering by alternate deposition of pure elemental Ni and Ni-25%Al layers in the range of 20nm - 120nm. By varying the substrate material and processing parameters such as deposition temperature, multilayers with two types of interfacial orientations, (111) Ni // (111) NiAl and (102) Ni // (002) NiAl, have been fabricated. Microstructural and phase characterization of multilayers in both plan view as well as cross-section geometries have been carried out using X-ray diffraction, SEM and TEM and the results of these will be discussed. Both orientations exhibited a high density of twins lying on the (111) planes. The loss of coherence in these multilayers as a function of the layer thickness will also be discussed. The fracture behavior of these multilayers has been studied by SEM fractography of the cross-section of specimens which failed as a result of the application of tensile stress. Interesting effects of the interfacial orientation and the layer thickness on the fracture characteristics of these multilayers will be discussed and an attempt will be made to rationalize the results based on the competition between yield and fracture in these materials as a function of applied stress. Finally, results of the deformation behavior of the Ni/NiAl multilayers, studied using nanindentation techniques, will be discussed and compared with the fracture studies.

4:30 P.M. V1.10
NANOMETER THICKNESS STUDY OF AMORPHOUS METAL MULTILAYERED THIN FILMS. J.B. Veiga, A.B. Mann, T.P. Veiga and R.C. Cammarata, Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD; C.L. Chien, Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD; H. King, Los Alamos National Laboratory, Los Alamos, NM.

The hardness and elastic behavior of amorphous metal multilayered thin films were investigated by nanoindentation. The samples studied were FeTi-CuNb, FeB-CuNb, and FeTi-FeB. The multilayered films were produced by sputtering onto Sapphire 0001 substrates. The range of bilayer repeat length studied was 2nm to 50nm, and the overall thickness of each film was about 1nm. Nanoindentation testing revealed that for each system, the hardness of the films was independent of the bilayer thickness, and corresponded to a rule of mixtures value calculated using hardness measurements of uniform films composed of the layer materials. This is in contrast to crystalline multilayered thin films which generally display significant hardness enhancements as the bilayer repeat length is reduced below 10nm. The implications and TEM observations regarding the deformation behavior of amorphous metals will be discussed.

4:45 P.M. V1.11

Resistance to thermal shock is an important design requirement for ceramic components which operate at elevated temperatures. This work describes a methodology developed to predict the thermal shock behavior of thin multi-layer ceramic systems (approx. 10 to 200um layers). An experimental procedure based on controlled specimen cooling has been devised to simulate the flow of a gas stream over the surface of the multi-layered system. Results of microstructural and fractographic investigations conducted on failed samples, including representative fracture patterns and crack initiation sites, are presented. A probability-based approach to predict the thermal shock behavior of the brittle multi-layer systems is undertaken and is based on (i) a weight function to measure the stress at failure, and on (ii) a weight function method and numerical (FE) analyses to formulate closed-form solutions for the stress intensity factors of interfacial cracks lying on a plane normal to the interface. Results are compared with those obtained from experimental and analytical studies. For a given failure probability, failure diagrams reveal regions of acceptable thermal shock conditions and geometric characteristics. Application to transient conditions typical of start-up and shut-down operation in solid oxide fuel cell applications are also given.

SESSION V2: METALLIC THIN FILMS
Chair: Peter M. Anderson and Oliver Kraft Tuesday, November 30, 1999 Room 308 (H)

8:30 AM V2.1
PLASTIC DEFORMATION IN THIN METAL FILMS. Sheffield P. Baker, Cornell University, Department of Materials Science and Engineering, Ithaca, NY.

It is well known that thin metal films may exhibit mechanical behaviors that are unlike those of bulk metals having the same composition. The differences are subtle but a number of features such as mechanical properties of bulk metals that are inherently metallic, but are not found in thin films. These differences can be attributed to the microstructure, which may be in a highly nonequilibrium form, and from dimensional constraints on deformation. Compared with bulk metals, the flow stresses in thin metal films are generally very high, and may be asymmetric, being different in tension and compression at the same temperature. Although models exist which can describe the strength of such films at room temperature in terms of constraints on dislocation motion, understanding of plastic deformation processes in thin films, particularly at elevated temperatures, is limited. In addition to very high strength at high temperatures, metal films may exhibit increasing flow stress with increasing temperature, negative yield stress effects (e.g. compressive plastic strains at yielding even though the applied stress on the film is tensile), and plastic memory effects (i.e. plastic strain–stress characteristics induced by a particular thermomechanical treatment persisting even after subsequent treatments to higher temperatures or strain levels). These effects have been seen to be very sensitive to low levels of impurities and to the presence and nature of adjacent substrate and capping layers. Plastic anisotropy is also expected to play an important role. To understand these behaviors, constraints on dislocation relaxation and dislocation motion have been invoked. In this talk, an overview of the progress in understanding the relationships among microstructure, geometry and plastic deformation in thin metal films will be presented and some implications for stress levels and reliability of devices containing metal films will be discussed.

9:00 AM V2.2
WAIVER CURVATURE STUDIES OF STRENGTHENING MECHANISMS IN THIN GOLD FILMS ON SUBSTRATES. O. Leung and William D. Nix, Stanford Univ, Dept of Materials Science and Engineering, Stanford CA.

The high strengths of gold thin films have been studied to examine the contribution of thickness and passivation effects on these properties. Wafer curvature/thermal cycling measurements have been used to study bare gold films ranging in thickness from 0.1 to 2.4 micrometers. Using FIB cross-sectional imaging and XPS analysis,
these films were found to have bare surfaces and a stable columnar grain structure after repeated thermal cycling. We found that the room temperature EMA in thin films is only affected by changes in the film thickness when the thickness is greater than about 1 micron. This relationship is expected from a dislocation structure model of plasticity. However, thinner films have stress substantially lower than this thickness would predict. Additionally, on unloading, these films show stress-temperature slopes not predicted by a simple dislocation model. The films were again measured after the piston was applied to the surface and allowed to cool. We found that the observed stresses are only minimally affected for films thicker than 1 micron. Thicker films were able to sustain much higher stresses, especially at elevated temperatures. This strengthening effect on thicker films is consistent with the strain contribution from the free surface of the film.

9:15 AM V.2.3
ACTIVATION VOLUME FOR INELASTIC DEFORMATION IN POLYCRYSTALLINE Ag THIN FILMS. Mauro J. Kobrinski and Carl V. Thompson, Massachusetts Institute of Technology, Dept. of Materials Science and Eng., Cambridge, MA.

It has been extensively reported in the literature that dislocation plasticity is important in metallic thin films on rigid substrates. However, the dominant mechanisms of dislocation plasticity are still not well understood. This work focuses on the low temperature (T \textless 200 °C) inelasticity of polycrystalline Ag thin films on oxidized Si substrates. We present experimentally determined values of the activation volume characteristic of inelastic deformations, as measured using two independent techniques: measurements of the rate of stress relaxation during isothermal annealing of thin film deposited on wafers, and in-situ TEM studies of dislocation dynamics in films deposited on top of micromachined membranes. The characteristics of the dislocation motion and the values of the activation volumes are consistent with a thermally activated motion of dislocations through forest-dislocation obstacles. The mean distance between obstacles for dislocation motion was found to be significantly smaller than the thickness of the film and grain size. An important increase in dislocation density with decreasing temperature was observed. The implications of these results in understanding thermally activated inelasticity and work hardening in thin films are discussed.

9:30 AM V.2.4
MECHANICAL PROPERTIES OF ELECTROPOLISHED COPPER THIN FILMS. R. Speckens1, C. Volkers1,2, K. Takashahi1, S. Fiorillo1, J. Miser1, and W. L. Brown3. Bell Labs, Lucent Technologies, Murray Hill, NJ.

In recent years several models have been developed that describe the increased yield stress of thin films as functions of grain size and film thickness. However, it has been difficult to separate the two contributions experimentally, as the maximum grain size is correlated to the film thickness by the Mullins criterion. In the case of aluminum thin films, a size-dependent grain orientation, no-migration was found to reduce film thickness without changing grain size. Chemical-mechanical polishing (CMP) has enabled us to separate the two components for copper, allowing us to reduce film thickness without changing grain size. Stress-strain curves were measured for two sets of electroplated copper films by a nanoindentation testing technique. The first set started with a thickness of 1.8 microns of recrystallized electroplated copper, was thinned to different thicknesses by CMP and subsequently annealed. For the second set, the order of the anneal and CMP thinning were reversed. Thus the first set had a variation in grain size as well as film thickness, whereas the second set only varied in film thickness. The mechanical properties were analyzed from the stress-temperature curves by extracting the tensile yield stress at room temperature as well as the area of the hysteresis of the temperature cycle up to 400°C. The grain size was determined by a focused ion beam (FIB) system and the texture by x-ray diffraction. The yield thickness was found to increase with decreasing film thickness for both sets of samples, as anticipated. The set that had been annealed before CMP showed a smaller stress-temperature hysteresis. This again was expected because of the smaller average grain size for this set of samples. Interpretation of these observations is complicated by the bidimensional grain size distribution originating from the recrystallization process at room temperature.

9:45 AM V.2.5

The Hall-Petch relationship for coarse-grained polycrystalline materials predicts that the hardness of a material should increase with decreasing grain size according to the equation \textit{H} = H_0 + \textit{Kd}^{-1/2}, where \textit{d} is the grain diameter and \textit{H}_0 and \textit{K} are constants. The result of this equation is a matter of debate with some experiments even showing a softening with decreasing grain size for sizes in the range of 5-10μm. To test the Hall-Petch relationship using a new method of sample preparation, we formed thin films of both Ni and Cu on silicon substrate by pulsed laser deposition (PLD). The PLD technique can produce very small granms, and transmission electron microscopy shows that the sizes in layers deposited at room temperature were 620 nm and 20-45 nm, respectively, for Ni and Cu. Using an indenter technique combined with an analysis based on finite-element modeling we then used to evaluate the mechanical properties of the layers. This analysis accurately determines the residual yield stress, Young's modulus, and hardness of the layers from indentation data, separating the properties of the films from those of the substrate. For room temperature deposited films, the measured hardnesses for Ni and Cu were 11.2±0.5 and 2.9±0.3 GPa, respectively. These hardnesses are higher than observed in layers with similar grain sizes made by other techniques, and are consistent with a simple extrapolation of the Hall-Petch relationship from coarse-grained material. The observations not only extend the Hall-Petch relationship to very small grain sizes, but also suggest that PLD layers have superior mechanical properties, perhaps due to a denser, more uniform microstructure than fine-grain materials prepared by other means. This work was supported by the US Department of Energy through their Office of Basic Energy Sciences under contract DE-AC03-76SF00098.

10:30 AM V.2.6
HYDROGEN-INDUCED PLASTIC DEFORMATION OF THIN FILMS. A. Pundt1, 2, U. Landsh"ahn1, U. H"ubener1,2, U. Geyer1, T. Wagner2, M. Getzlaff2, M. Bode3, R. Wiesendanger9,9, R. Kirchheim1.

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Deviations in the mechanical behavior of a thin film that is clamped to an elastically hard substrate, compared to bulk metal can be studied by absorbing hydrogen in thin films. Since hydrogen is dissolved in interstitial sites and exerts forces on neighboring metal atoms, the in-plane stresses increase with increasing hydrogen concentration. In the case of Ni films that were covered with a thin Pd layer, stresses of several GPa were measured. Nb and Gd films prepared by electron evaporation were loaded with hydrogen. Oxidation of surface and in-plane stresses during electrohydrodynamic loading were determined by performing x-ray diffraction and substrate bending measurements. At low H-concentrations the developing stresses are in agreement with a clamped film expanding elastically out-of-plane only. Above a critical H-concentration the films deform plastically. In some cases the critical hydrogen concentration corresponds to the terminal solubility, above which the hydride precipitates by emission of extrinsic dislocation loops. For the remaining cases a critical stress is reached before passing the phase boundary, which leads to the formation of misfit dislocations at the interface between film and substrate. The concomitant glide lines of these rejection lines were observed on the surface of the film by using Scanning Tunneling Microscopy. Additional surface pattern were observed that can be correlated with emitted dislocation loops.


11:00 AM V.2.7
EFFECTS OF UNDERLAYER COMPLIANCE ON FLOW STRESS IN AI THIN FILMS. Seungmin Hyan, Richard P. Vinci, Lehigh Univ., Materials Science and Engineering, Bethlehem, PA.

The stress behavior of Al thin films on Si was investigated by the X-ray diffraction technique. The influence of a compliant underlayer was explored by depositing the Al on a variety of underlayers such as polyimide. The polyimide underlayer was deposited by spin coating, then thermally cured. Thickness was controlled by varying the amount of N-Methylpyrrolidone (NMP) based solvent. Several samples also had an LPCVD silicon nitride interlayer between the polyimide and the Al. The aluminum films were deposited by magnetron sputtering to a thickness of 1μm. The influence of underlayer thickness and compliance on the flow stresses of the Al thin films has been determined. The results are compared with predictions based on image dislocation forces in the adjoining layers.

11:15 AM V.2.8
PLASTICITY IN Cu THIN FILMS. Volker Weihmann, Winfried Brederer, Institute of Solid State and Materials Research Dresden, GERMANY.

A detailed study about the plastic behavior of thin Cu films with...
The formation of silicides is a critical process step in current MOS technologies, since they are the contact material between the doped Si and the metal, and provide the link between the transistors and the interconnections. Although the scaling of silicides in MOS technologies has been mainly discussed in view of resistivity, it has become clear over the recent years that the mechanical stress induced in it plays an important role. In this paper, silicide induced stress build up will be presented in view of materials and process choices. The impact of stress on the technology will be discussed as it will play an important role in the scalability of the device.

2:00 PM V3.2
EXCESS VACANCY GENERATION BY SILICIDE FORMATION IN Si. R.J. Jacobsen, Lehigh University, Bethlehem, PA.

It has long been recognized that excess point defects are generated when a metal silicide is formed on silicon. Since the common dopants diffuse in Si with the aid of both self-interstitials and vacancies, these point defects affect the performance and reliability of the device. In the adjacent vicinity, TiSi2 is known to enhance the concentration of vacancies and several mechanisms have been proposed for this effect. Recent literature has dealt with and rejected many of these ideas; however, some of the remaining few like film strain and lattice contraction upon silicidation have been the subject of state of the art experiments which has led to their rejection. It is the contention of this paper that by using the experimental data from this recent work and reinterpreting it, the model of volume contraction of the silicides as the cause for vacancy injection still represents the most physically satisfying cause and therefore, was mistakenly rejected. A brief discussion of relevant mechanisms for vacancy generation will be given.

2:15 PM V3.3
SEQUENTIAL OPERATION OF THREE DISTINCT MISFIT DISLOCATION INTRODUCTION MECHANISMS IN AN EPITAXIAL BILAYER FILM. Vidyut Gopal, E. P. Kwon, Purdue University, Materials Engineering, W. Lafayette, IN; Ee-Hung Chen, Jerry M. Woodall, Yale University, Electrical Engineering Department, New Haven, CT.

Mismatch stress relaxation mechanisms in bilayer films of [In/Al] on InAs on GaP have been studied. Initial edge (6|3|1) misfit dislocations at the InAs/GaP interface appear to be introduced directly at island edges during initial stages of growth. The incomplete mismatch compensation is taken up by the introduction of mixed (6|3|1) dislocations, usually in pairs which combine to form edge dislocations. The edge dislocations in the interface then move laterally to equalize their spacings. The upper (In/Al) as capping layer, which is tensile strained to match the reduced InAs, exhibits a different mechanism of misfit relaxation. The dislocations are confined to the interface and move by glide, directly introducing sessile edge dislocations at the buried interface. It is believed this is the first time this mechanism has been observed.

2:30 PM V3.4
Si1-xGe x HETEROEPIXY ON PATTERNED SUBSTRATES. Congqi Su, Okike, Applied Micro Circuits Corporation, Process Development Division, San Diego, CA.

Graded Si1-xGe x heteroepitaxial thin films grown by low pressure chemical vapor deposition on patterned Si substrates were investigated with regard to their mechanical properties, poly-Si1-xGe x/epi-Si1-xGe x interface structure and the dependence of the growth process characteristics on the substrate crystallographic orientation. The heterostructures were characterized by transmission electron microscopy for morphology and defects, by secondary ion mass spectrometry for in-depth chemical profiling, while XRD revealed epitaxial growth on single crystal Si structures. The film growth over single crystal Si regions can be strongly affected by the surface of the substrate crystallographic orientation. In such cases, the growth rate of the film was observed to be a function of the crystallographic orientation of the growth surface. Furthermore, non-planarity leads to the formation of facets which can result in further defect formation in the film.

2:45 PM V3.5
STRESS RELAXATION IN UNIAXIALLY ORIENTED SiGe/Si EPITAXIAL LAYERS. Morgan Warr, Herbert Nemerov, North Carolina State University, Physics Dept, Raleigh, NC.

The relationship between equilibrium lattice spacing and phonon frequency makes Raman spectroscopy ideal for examining strain in epitaxial heterostructures. The 4-phonon transition for the Ge face centered cubic structure allows thin epitaxial layers of SiGe to be studied.
Si(x)Ge(1-x) to be grown compressively strained to the lattice spacing of the Si substrate for low x. This strain can be relieved by two main methods. One is to simply grow the layers thick enough so that the strain overcomes the interfacial bonding force and defects form of the layer assume its natural spacing. The other is to grow a thickness where the layer on the verge of relaxing, then anneal to supply the necessary energy to force the lattice to relax. We have grown samples with x = 0.3 on Si substrates with unique orientations to examine the relaxation. The crystallographic orientations of the substrates used were off-axis from the (001) plane towards the (111) plane by 1° and 2°, respectively. In Delphi and Lin we have seen shifts of up to 5 Wavenumbers between the relaxed and unreleased states in the Si-Si mode of the epilayers. The unrelaxed samples showed considerable surface roughening as seen in AFM regardless of their size of strain before annealing.

3:30 PM V3.6
COHERENT AND INCOHERENT PLASTIC RELAXATION IN HHL HETEROSTRUCTURES. André Bender, Émilie Smocz, CEMES, CNRS, Toulouse, France.

The plastic relaxation to has been studied by HREM experiments for large lattice mismatch systems such as GaSb/GaAs and GaAs/InP. The micrographs have been treated by phase method analysis in order to evaluate the degree of relaxation at the level of the interface. The GaSb/GaAs optimal system has been obtained, in the best conditions of epitaxy, with an interface constituted by a perfect square array of Lomer dislocations. GaSb appears to be fully relaxed and well organized. This perfection is attributed to the GaSb island growth of the coherent layers in the network creating the well organized misfit dislocations network. The GaAs/InP system has been grown at 450°C in order to obtain both a uniform thickness and good crystalline quality of the GaAs epilayer. Some nanotubes able to inter-act GaSb layer to be relaxed by a network of randomly distributed partial and 60° dislocations segments with a limited length. At low growth temperature, the plastic relaxation appears directly at the growth front when the interdiffusion atonic lines take a position different from the ideal pseudomorphic one. In this case, the relaxation mechanism is incoherent.

3:45 PM V3.7

Typical III-nitride semiconductor thin films have complex microstructures that can be characterized either as noisy epitaxy, or as two highly oriented polycrystals. We have used real-time length measurement during chemical vapor deposition of GaN on sapphire and AlGaN on GaN, combined with ex situ x-ray characterizations, to determine the evolution of dislocations. We find that GaN grows in tension, which is unrelated to epitaxial effects, but may result from the elimination of free-volume defects such as holes. AlGaN also exhibits a network of dislocations and coherent AlGaN films grown coherently on GaN. Due to the lattice mismatch, coherent AlGaN on GaN is in a state of tensile stress. At some critical thickness, a brittle/ductile failure mode occurs, exhibiting a high density mud-crack network combined with a high density of interfacial microcracks and dislocations. We speculate that cracks are necessary in order to permit facile introduction of dislocation glides, but this remains to be proven. Finally, the stress relaxation kinetics can be gradual or discontinuous, depending on the amount of stored elastic energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

4:00 PM V3.8
STRESS EFFECTS ON THE OXIDATION OF PLANEAR SiO2 THIN FILMS. T.D. Delphi and R.J. Jaccodine, Depts. of Mechanical Engineering and Materials Science, Lehigh University, Bethlehem, PA.

The oxidation kinetics of SiO2 thin films are thought to be strongly affected by the mechanical stresses generated during the oxidation process. These stresses arise because of the fact that a molecule of SiO2 occupies approximately two times as much volume as an atom of Si. Because almost all of the expansion brought about by volume change takes place normal to the plane of oxidation, it is commonly thought that normal oxidation serves as a sort of reference, stress-free configuration. Experimental evidence has consistently indicated, however, that this is far from the case. Planar specimens from which oxide has been removed or added to one side have developed numerous microcracks, indicating large in-plane stresses induced by the oxidation process. Delphi (J. Appl. Phys. 6, 574, 1998) has interpreted this phenomenon in terms of an intrinsic strain, that is, a small component of expansion strain in the plane of oxidation. Fits to the experimental data of Kolesov and Irene (J. Appl. Sci. Tech. B 6, 574, 1998) have yielded a value of 6° in-plane component of strain of approximately 0.002. Even though this value is three orders of magnitude smaller than the strain component normal to the plane of oxidation, the fact that it is strongly restrained by the underlying silicon substrate can lead to in-plane stresses on the order of several hundred megapascals. Delphi and Lin have recently analyzed the effects of these stresses upon oxide diffusion in planar films. One of the interesting consequences of this study is that oxide stresses in SiO2 can be modeled as a parabolic coefficient in the Delphi-Grove model may be as much as 10% in error as a consequence of in-plane stress effects. Recently, Mihaly, Jaccodine, and Delphi (Appl. Phys. A, 1999) have examined the growth of very thin oxides upon silicon striga loaded in four-point bending. Under these conditions, the oxide film is subjected to an externally imposed in-plane constant of constant magnitude. It was found that compressive in-plane stress had an unambiguous retarding effect upon oxide growth, whereas tensile stresses had an uncertain effect. For oxides in this thickness range, the oxidation kinetics are thought to be governed by the rate of the oxidation component. Hence these results imply that in-plane stresses affect the oxidation reaction rate. This finding goes counter to a widely accepted model for the effect of stress upon the reaction rate.

4:15 PM V3.9
PHASE FORMATION AND MECHANICAL PROPERTIES OF MULTIPHASE CARBIDE COATINGS. J.E. Krzczonowski, S. Koutskis, Mechanical Engineering Dept., University of New Hampshire, Durham, NH, D. J. M. Davies, Dayton OH, J.S. Zobinski, Wright Laboratories/Materials Directorate, Wright-Patterson AFB, Dayton OH.

Hard carbide coatings are widely used to improve wear resistance and fatigue resistance in rolling contact applications. To further improve the performance of these coatings, we are investigating the potential of nano-structured multiphase coatings consisting of mixed carbide components. We have conducted experiments on two ternary cubic systems, Ti-Mo-C and Ti-Si-C. According to available phase diagram data, the Ti-Mo-C system exhibits substantial, but not complete, solubility of Mo in TiC, while the Ti-Si-C system TiC and SiC are essentially insoluble. Coatings in these systems were fabricated by co-sputtering from carbide targets, allowing complete range of film compositions to be obtained in each system. The films were deposited on steel and sapphire substrates at temperatures ranging from room temperature to 600°C. Film compositions were determined using XPS, and X-ray diffraction was used to examine the films for texture, grain size, phase stability and the potential for creating nano-structured multiphase films. Generally, the films deposited on steel exhibited a stronger [111] orientation in comparison to films deposited on sapphire. Mo was found to be soluble in TiC up to about 8 mol.%, and between 80-90 mol. % a multiphase structure was obtained. The hardness of these films generally did not improve due to the Mo additions. For the Ti-Si-C films, X-ray diffraction results were consistent with the formation of cubic SiC and TiC phases. In these films, the hardness was found to improve with SiC additions by a factor of 3-4 times compared to films with only TiC. The optimal composition for hardness enhancement is near 10% SiC in TiC. Addition experiments are underway to explore the tribological properties of these films.

4:30 PM V3.10

Mechanisms based models predict that TiN-TiB2 composite films can have a hardness comparable to diamond if an optimum microstructure is obtained. The superhardness results from the dispersion hardening effects of nanoscale particles. In this paper, we report on the effect of annealing on the hardness of TiN-TiB2 co-precipitated films. These films were sputter deposited on sapphire substrates in a dual-opposed cathode unbalanced-magnetron sputtering system using TiN and TiB2 ceramic targets. The variable speed rotating substrate holder alternatively faced the two targets. The volume of TiN fraction was varied from 20% to 85% by adjusting the relative power on the two targets. The 1 micron films were annealed at temperatures > 500°C in a nitrogen atmosphere. The as-deposited and the annealed films were characterized using x-ray diffraction, transmission electron microscopy, and microindentation. Preliminary experiments indicate that the hardness of the as-deposited films is higher than that of the as-deposited films and the rule-of-mixtures values. The change in the mechanical properties will be related to the microstructural changes and the results compared to model predictions.
The tensile stress generation in evaporated metallic thin films growing in the Volmer-Weber mode is frequently associated with nucleation of discrete islands to form nascent grain boundaries. We have performed careful in situ stress measurements during UHV deposition of Al for determining Si$_2$O$_5$ microstructure and characterizing the stress evolution as a function of deposition temperature and rate. These measurements are supported by extensive ex situ characterization of the microstructural evolution in wedge-shaped films. Copious island coalescence and grain boundary formation did not initially influence stress generation. We will argue that this represents uncontrolled boundary formation where lack of stress constraints permit relaxation of the stress. It is only beyond the percolation threshold that significant tensile stress generation occurs as sterically-constrained grain boundaries form by a lateral sticking process. We will attempt to quantitatively correlate the kinetics of constrained boundary formation with the observed tensile stress evolution. The role of grain growth in tensile stress generation will also be discussed.

SESSION V4: POSTER SESSION
Chairs: Paul R. Beser and Oliver Kraft
Tuesday Evening, November 30, 1999
8:00 P.M.
Exhibition Hall D (H)

V4.1 EFFECT OF ANNEALING ON MICROSTRUCTURE AND PROPERTIES OF Al-Ti MULTILAYERED FILMS R. Mira,1 A. Madsen,2 R. Hoffman3 and J.R. Weertman1. 1Department of Materials Science and Engineering, Northwestern University, Evanston, IL 2Advanced Coating Technology Group, Northwestern University, Evanston, IL.

Al-Ti multilayered films were deposited by magnetron sputtering of Al and Ti target in UHV. Si$_2$O$_5$ and CuO substrates. The substrates were alternately passed under Al and Ti to obtain the desired multilayers. The bilayer thickness was 16 nm with Ti constituting 12% of the total thickness. The films (1.7 µm thick) were annealed at 400°C for 0.72 T$_m$ of Al for periods between 1 and 24 h. In course of the annealing, interdiffusion and chemical reaction between Al and Ti layers led to the precipitation of Al$_3$Ti particles. Plan view and cross-section TEM examination of as deposited and annealed films were performed to study the microstructural evolution, and to estimate the Al grain and Al$_3$Ti particle size distribution. Cross-section TEM and X-ray diffraction showed well-defined layered structure in as-deposited films. The microstructure was found to be metastable in the first 6 h of annealing, with Al-Ti multilayers being gradually replaced by Al$_3$Ti composite structure. X-ray and electron diffraction analyses showed that Al$_3$Ti possessed the DO$_{22}$ structure. Nanocrystalline hardness values of as-deposited and annealed films (on Si substrates) were higher than those of pure Al or Ti films. The hardness increased on annealing for periods up to 6 h, followed by an increase between 6 and 8 h of annealing. The enhanced hardness in as-deposited condition can be due to interfaces hindering dislocation motion in the Al$_3$Ti layered structure. The layered structure degraded in the initial periods of annealing, leading to decrease in hardness. Subsequently, the hardness increased with an increase in volume fraction of Al$_3$Ti precipitates. The hardness showed only minor variation between 8 and 24 h, implying presence of a relatively stable microstructure after 8 h of annealing at 400°C. Further research is in progress on study of the mechanical properties of these films, and will be reported.


The hardnesses and elastic moduli of aluminum nitride (AlN) and titanium nitride (TiN) sub-micron thin films were measured using nanoindentation based on a continuous stiffness measurement (CSM) technique. Thin film thicknesses, based on profile measurements of simultaneous as-grown step samples, were 210 and 180 nm with surface roughnesses of 12 nm and 2 nm for AlN and TiN, respectively. X-ray diffraction showed AlN as a highly textured polycrystalline AlN wurtzite structure with a (0001) orientation and TiN as a cubic structure with a (111) orientation. The CSM technique provided hardness and elastic modulus as a function of depth. Finite element modeling (FEM) aided in determining the optimum indenter contact depth at which the thin films behaved as a semi-infinite solid with negligible substrate induced artifacts. Hardnesses of TiN and AlN were determined analytically, 25 GPa and 33 GPa, as compared to FEM results of 24 GPa and 30 GPa, respectively. The elastic moduli measured 320 GPa and 370 GPa for these AlN and TiN thin films, respectively.

V4.3 STRESS RELAXATION AND MOSAIC STRUCTURE IN Si$_2$Ge$_3$ EPILAYERS GROWN ON Si(001) SUBSTRATES. H.J. Li, Physics Department, University of Houston, Houston, TX and Institute of Physics, Chinese Academy of Sciences, Beijing, CHINA.

X-ray double- and triple-axis reflectometry have been employed to study the strain relaxation and the mosaic structures in molecular-beam epitaxy grown Si$_2$Ge$_3$ epilayers on Si(001) substrates with a low-temperature buffer. The thickness of the Si$_2$Ge$_3$ layers ranges from 800 to 5900 Å. Degrees of strain relaxation of these films were found ranging from 5 to 90%. For samples with a lower degree of strain relaxation, the x-ray rocking curves contain two components: a narrow one on top of a broad one, whereas for samples with a higher degree of strain relaxation, the x-ray rocking curves show a single peak. Detailed analyses suggest that the narrow peak in the two-component rocking curve is due to Bragg diffraction from nearly perfect regions in the film, while the broad (more diffuse) one is caused by the dislocation-induced mosaic structure. This indicates that at early stages of strain relaxation, the film contains mosaic structures later separated by perfect regions. These occur because the strain is not relieved entirely and is effectively localized in a lateral range of about the layer thickness. Therefore, far away from the dislocations, the film is unaffected and is more perfect. With the increasing in the degree of strain relaxation, and consequently in the dislocation density, the mosaic regions of the layer expand while the perfect regions shrink and finally vanish completely. By making detailed analyses of the rocking curve profiles, we are able to estimate the volume fraction of the mosaic or distorted regions in the film. A criterion for the appearance of two components in the rocking curve or the coexistence of the perfect regions and distorted regions in the film is given in terms of Al and Ti being components of the layer thickness. Moreover, our results show that, in our case, the conventional method of estimating dislocation density from the x-ray rocking curve width fails. Work was partly supported by NSF of China under Grant No.19834050. The author acknowledges Texas Center for Superconductivity at University of Houston (TCSUH) for financial support.

V4.4 RADIO SPECTROSCOPIC STUDY OF STRAIN AND DISORDER IN SURFACANT-MEDIATED MBE GROWN Ge(211)/Si(001) G. Beil, S. Sivananthan, Microphysics Laboratory, University of Illinois at Chicago, Chicago, IL; Y. Gogotsi, Dept. of Mechanical Engineering, University of Illinois at Chicago, Chicago, IL.

Due to the presence of a 4.2% lattice mismatch between Ge and Si, Ge is known to grow via the Stremkoe-Krsticov growth mode (2D followed by 3D) unless the surface free energy of the growing layer is sufficiently altered by a surfactant. Many groups have shown that the deposition As, Te, Bi, or Sb during Ge deposition, layer-by-layer growth can occur to a much greater thickness than the critical thickness of 3 monolayers in both the (001) and (111) orientations. Furthermore, it is seen that the surfactant acts to suppress Ge-Si alloy formation at the interface. In this study, we have grown thin Ge layers on Si(211) substrates with and without As deposition before Ge growth to study the effect of surfactant mediated growth in the (211) orientation. The layers were monitored in situ by reflection high-energy electron diffraction (RHEED) and were characterized ex situ by Raman spectroscopy. Preliminary results confirm that the growth rate is altered significantly by exposing the Si(211) surface with As prior to Ge growth. Measurements of peak shifts and peak widths in the Raman spectra show that more disorder and alloying are present for layers grown without the surfactant. However, alloy formation is not completely suppressed for layers grown with the aid of a surfactant, contrary to Ge grown in the (001) orientation. These results, as well as a preliminary growth model will be discussed.
Moisture penetration is known to be the main factor which influences the lifetime of organic electroluminescent (EL) devices. Hence, a passivation layer is indispensable for protecting the organic EL device from moisture penetration. EL device fabrication processes having characteristics such as high electrical resistance, high barrier for moisture penetration, and low mechanical stress are required to be formed at a low temperature below 100°C. In this study, amorphous silicon oxide/nitride (SiON) films were deposited in a room temperature using a sputtering-type ECR plasma system. SiON films were deposited as a function of flow rate ratio of O2 to N2 at a constant Ar flow rate under the condition of a microwave power of 500 W and a radio frequency power of 500 W, to ECR plasma and to an ionization target for sputtering, respectively. The chamber gas pressures were in the range of 1.1-1.3 mTorr during the deposition processes. In addition to the deposition rate for each condition, films were characterized by measuring refractive index, chemical composition, electrical resistance, and stress. The structural properties of the deposited films were investigated using FTIR and XPS. Also the adhesion of water in the deposited films was evaluated by thermal desorption spectroscopy (TDS). It was found that the characteristics of electrical resistance, density, and internal stress of the films largely depend on the gas flow rate ratio of O2 to N2. High electrical resistance, high density, and low stress amorphous films could be formed as an optimum condition, under which the SiON film had a refractive index of 1.6. The results of TDS measurements showed that the SiON film had a higher barrier against moisture penetration relative to deposited SiO2 and SiN films. In addition, the graphs showed high low stress resistance characteristics. These results indicate that the SiON film deposited using a sputtering-type ECR plasma has the potential to be utilized as a passivation layer of devices such as organic EL, which are required to be formed at low temperature.

**V.4.6 VISCOS FLOW IN DOPED AMORPHOUS SI AND PURE AMORPHOUS Si-THIN FILMS. Jennifer A. Molloy, Fei Spreeg, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA.**

Stress relaxation by Newtonian viscous flow was observed in spatter-deposited, doped amorphous Si and evaporated amorphous Si thin films. The stress was determined from substrate curvature measurements using a laser scanning technique. Gold and boron were introduced into the a-Si films to determine if there is an effect on the viscosity. It is known that these impurities enhance self-diffusion and epitaxial regrowth in a-Si. The temperature dependence of and effects of structural relaxation on the viscosity of a-Se thin films will be presented. Photoeffects on the viscosity of a-Se are being explored.

**V.4.7 PREFERRED ORIENTATION CONTROL OF PLATINUM THIN FILMS DEPOSITED BY DC MAGNETRON SPATTERING USING Ar2/N2 GAS MIXTURES. Dong-Soo Lee, Dong-Yeon Park, Hyun-Jung Woh, Jowoon Ha, INOSTEK, Inc., Seoul National University, Seoul, KOREA; Ruiyoush Yoon, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA.**

The properties of ferroelectric oxide films can be tailored by controlling their preferred orientations. For example, strongly (100)-oriented ZnO thin films can be grown on Si(100) substrates using pulsed laser deposition. Various models for the preferred orientations of such films have been proposed. In this study, a new model was presented in which the ZnO films have a preferred orientation of the c-axis perpendicular to the surface. The films were deposited by reactive magnetron sputtering using an Ar2/N2 gas mixture. It was found that the preferred orientation of the c-axis is associated with the presence of a nickel substrate. However, the preferred orientation of the c-axis is not observed on a Si substrate. This indicates that the preferred orientation of the c-axis is a property of the Ni substrate, rather than the ZnO film itself. The preferred orientation of the c-axis is a function of the deposition rate and the gas flow rate ratio. The results suggest that the preferred orientation of the c-axis is a result of the growth mechanism of the ZnO film on a Ni substrate.

**V.4.10 INFLUENCE OF THE DEPOSITION PARAMETERS ON THE ELECTRICAL AND MECHANICAL PROPERTIES OF PHYSICALLY DEPOSITED IRIDIUM AND RHODIUM THIN FILMS. Saim Gojoki and Margaret Eagan, AlliedSignal, Inc., Morris, NJ.**

Iridium and rhodium are metals which possess attractive properties for use as electronic conductors in various devices. These elements are chemically inert, have relatively high intrinsic electrical conductivities and elastic moduli and acceptable thermal expansion coefficients. The electrical and mechanical properties of these films depend on the deposition parameters, such as temperature, deposition rate, and film stress. The results of this study suggest that the deposition parameters have a significant influence on the electrical and mechanical properties of the iridium and rhodium films. The deposition parameters can be controlled to obtain films with desired properties, such as high conductivity and low stress, for use in electronic devices.
V4.11 MICROSTRUCTURAL EVOLUTION IN COPPER FILMS UNDERGOING LASER PULSATING AT HIGH PRESSURES.
R. Jukkuri, C.D. Dobson, A.L. Greer, Dept. of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK.

The current technologies for fabricating multilayered metallization are likely to be inadequate on account of the high aspect ratio and complex geometries. We have developed a technique involving sputtering and laser pulling for filling high-aspect ratio vias with Cu. The results of the extent of via filling are presented in a companion paper. Microstructural evolution in the Cu films is investigated in this paper. Cu films are deposited by sputtering over an oxidized Si substrate and etched by array etching of holes with different aspect ratios. The Cu film is of a thickness (1.5 μm) such that it bridges over the via holes. The wafer is then subjected to laser pulling along with an application of a pressure of 70 Mpa. The microstructures of the films and the effects of laser pulling on X-ray diffraction, focused ion beam microscopy (FIB) and cross-sectional TEM. The FIB images of the film show a checkerboard pattern of grains replicating the square pattern of vias holes underneath. We explain the checkerboard-on-the-basis of the melting of the film under laser pulsing and subsequent solidification wherein each via hole acts as a nucleation site and has a crystal associated with it. The TEM images of the films show extensive dislocation activity in the film. Even though the sputtered films have a < 111> fiber texture, the subsequent texture evolution is dependent on the applied pressure. The role of pressure in dictating the dominant texture will be discussed.

V4.12 THE INFLUENCE OF THERMAL HISTORY AND ALLOYING ELEMENTS ON TEMPERATURE-STRENGTHENING OF THIN FILMS.

Stress is an important parameter in determining the performance of thin films in many applications. Stresses can be influenced by the addition of small amounts of alloying elements. To understand the influence of alloying elements on stress, we have studied the influence of TiN Al films with different compositions. The stress relaxation depends on thermal processing, and the stress relaxation increases with increasing Cu concentration. The stress relaxation is not as clear as in Al or AlN films, where stress relaxation occurs without any thermal processing. Raising the stress relaxation is achieved by increasing the concentration of Cu in Al films.

V4.13 IN SITU STUDY OF DISLOCATION BEHAVIOR IN COLYNAR AI THIN FILMS ON SI SUBSTRATE.
Charles W. Allen, Materials Science Division, Argonne National Laboratory, Argonne, Illinois; Herbert Schneider, Institut fur Festkorperforschung, Forschungszentrum Julich GmbH, Jiilich, GERMANY, Jan M. Hiller, Madison Area Technical College, Madison, WI.

In situ transmission electron microscopy (300K) has been employed to study the evolution of dislocation microstructures during thermal cycling of a 200nm Al thin film on a thick Si substrate. After a few thermal cycles between 150 and 550°C, stable columnar grains of the Al were established with lateral sizes ranging from 2 to 20 μm. On rapid cooling (~5°C/sec) from 500°C, dislocations form complex arrays at 360-380°C, quickly multiplying and forming complex arrays on further cooling. Damage effects associated with a 300K electron beam appear below 150-170°C. From a large number of such experiments we have attempted to deduce the dislocation evolution during thermal cycling for these particular Al polycrystalline arrangements. Such results are expected to be a good test of any model for plastic metal relaxation during thermal cycling in this multilayered system. Work supported by U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

V4.14 DIFFUSIONAL HILLOCK FORMATION IN Al THIN FILMS CONTROLLED BY CREEP.
Deekshee Kim1, William D. Nix2, Eduard Arzt3, Michael Denl1, James D. Plummer1; 1 Center for Integrated Systems, Department of Materials Science and Engineering, Stanford University, 2 Max-Planck-Institut fur Metallforschung, Stuttgart, GERMANY.

Thermal hillocks in sputter-deposited Al films have been studied as a part of a broad study of creep-induced diffusion processes in Al. The Al films were annealed for 2 hours at 540°C in forming gas. The median grain size of the deposited Al film was 9um; the grain size increased to 98um after annealing. Traces amount of the impurities Ti and Fe were included into the Al film during deposition, as indicated by EDS. Stress measurement during thermal cycling, using the wafer curvature method, showed that the Al films were very strong; this finding was corroborated by hardness measurements. The microstructure of hillocks was examined by TEM and FIB. These micrographs show that hillocks start to form at the Al/SiO2 interface and grow under the original Al film. In some cases, the film fails as hillocks grow completely through the original film, with its columnar grain structure. The Al film on top of the hillocks appears to inhibit hillock growth by creating a back pressure associated with power law creep of the film. We modeled this formation of hillock formation by modifying boundary conditions of Chandrak’s hillock model. Our model gives hillock formation by different stresses in the surrounding area into isolated hillocks, assuming that the original Al film on top of hillocks, with its columnar grain structure, deforms following power law creep. Our model is applied to many different situations by using different creep laws for the top Al film.

V4.15 PLASTIC AND ELASTIC BEHAVIOR OF SPUTTER-DEPOSITED Cu/TiN BILAYERED FILMS BY NON-OXIDATION.
Eiji Kusuo, Yoshihito Sawahara, Naoto Kikuchi, Akira Kimbara, Kanazawa Institute of Technology, Matto, JAPAN.

Effects of metal underlayer thickness on plastic and elastic energies dissipated during the stressing leads process in a nonoxidation have been investigated for the film with a layer system of a hard top layer of TiN (Young’s modulus of 250-300GPa) and a soft underlayer of Cu (Young’s modulus of 10-140GPa). The bilayer films were deposited on alumina-silicate glass substrate by dc magnetron sputtering using an ultrahigh vacuum apparatus. The thickness of the TiN top layer was 25nm, while that of the Cu underlayer was varied from 0 to 500nm. Nonoxidation measurements were carried out by using a three faced pyramidial diamond stylus for maximum loads of 2.94, 4.90, and 6.86mN. The nonoxidation depth was 10% of the TiN layer thickness for all stress loads. It is found that the microhardness decreases slightly with increasing Cu layer thickness for all maximum loads and that the plastic energy increased monotonically with increasing Cu layer thickness, while the elastic energy slightly decreased with increasing Cu layer thickness. The elastic energy was more remarkable at a higher stress load. The ratio of energy dissipated to applied energy was approximately increased with increasing Cu layer thickness. This increase in the energy ratio implies that the film becomes more plastic with increasing Cu underlayer thickness. It is concluded that the increase in the thickness of the soft Cu underlayer influences plastic behavior more than elastic behavior of the film and that the contribution of the thickness change to the plastic and elastic behavior can be explained by the difference in the moduli of the two materials.

V4.16 SURFACE MODIFICATIONS DUE TO HYDROGEN INDUCED PLASTIC DEFORMATION OF Ga FILMS.
A. Pandi1, M. Getzlaff2, M. Bode3, R. Wiesendanger4, R. Kirchheim1; 1 Institut für Materialphysik, Universität Göttingen, Göttingen, GERMANY, 2 Institut für Angewandte Physik, Universität Hamburg, Hamburg, GERMANY.

During hydrogen loading of thin films that are clamped to elastically hard substrates, high in-plane stresses can occur. In case of thin Ni films stresses of several GPa were measured. To release stresses the film can deform plastically. In thin films plastic processes, i.e. by the formation of dislocations, should result in surface modifications. The role of the surface modification of epitaxial Ga films during hydrogen loading was studied on the nanometer scale by performing in-situ Scanning Tunneling Microscopy. Above a certain amount of hydrogen surface modifications appear in localized areas. Twenty percent features were found as epitaxial islands in in-plane stress fields. These surface patterns can be attributed to two different kinds
of hydrogen-induced plastic deformation processes. The disc islands appear in the concentration range where GHz precipitation is expected and are attributed to the formation of extrinsic dislocation loops. The slope field is attributed to a glissile step of a misfit dislocation near the film-substrate interface. Increasing the hydrogen content leads to a spread out of the localized surface pattern regions indicating a growth of the GHz precipitation according to the lever rule. At high hydrogen concentrations the surface of the Gd film is covered with a pattern of straight lines. This pattern appears oriented to the Gd film and can be attributed to elongated misfit dislocations.

V4.17 MECHANICAL PROPERTIES OF ALUMINUM THIN FILMS AS MEASURED BY BULGE TESTING. Yinmin Wang1, Richard L. Edwards2 and Kevin J. Hemker1,3; 1Department of Materials Science and Engineering, 2Applied Physics Laboratory, 3Department of Mechanical Engineering, Johns Hopkins University, Baltimore MD.

Free-standing rectangular Al thin films have been fabricated using sputter deposition and standard micromachining techniques. Mechanical properties and residual stresses of both as-deposited and annealed Al films were measured by bulge testing. The films were loaded into the plastic deformation regime, and then unloaded and reloaded several times. The pressure and deflection of the thin films were recorded and used to generate stress-strain curves. The plastic-strain elastic modulus, flow stress and plastic behavior of the Al thin films were used to characterize the mechanical response of these films. The Al films were measured to have a single-strain modulus that is slightly lower than the literature values for a [111] textured film. The Von-Mises yield stress was measured to be higher in the annealed films but much more significant strain hardening was observed in the as-deposited films. A plastic hysteresis was observed on unloading and reloading stress-strain curves of the as-deposited Al films but not the annealed films. Possible mechanisms for differences in flow behavior of these films will be discussed.

V4.18 CAN STRESS-SRAIN RELATIONSHIPS BE OBTAINED FROM INDENTATION CURVES USING CONICAL AND PYRAMIDAL INDENTERS? Yang-Tse Cheng, General Motors R&D Center, Warren, MI; Che-Ming Cheng, Institute of Mechanics, Beijing, CHINA.

Applying the scaling relationships developed recently for conical indentation in elastic-plastic solids [1,2], we examine the question of whether stress-strain relationships of such solids can be uniquely determined by matching the calculated loading and unloading curves with that measured experimentally. We show that there can be multiple stress-strain curves for a given set of loading and unloading curves. Consequently, stress-strain relationships may not be uniquely determined from loading and unloading curves alone using a conical or pyramidal indenter.


V4.19 MEASUREMENT OF RESIDUAL STRESSES BY LOAD AND DEPTH SENSING SPHERICAL INDENTATION. Ercan Tugberk, STEEL Group, Turin, ITALY; George M. Pharr, Univ of Tennessee, Dept of Materials Science and Engineering, Knoxville, TN, and Oak Ridge National Laboratory, Metall and Ceramics Div, Oak Ridge, TN.

The finite element method was used to determine whether load and depth sensing indentation with spherical indenters may be useful in the measurement of residual stresses in materials. The spherical indentation process for a wide range of elastic/idependent materials to which compressive and tensile biaxial stresses were applied was simulated using standard finite element techniques. The elastic moduli and yield stresses of the materials were varied systematically to model the behavior of a variety of materials. The elastic/idependent materials were considered, with the residual stress levels varied from zero up to the yield stress. All three indentation regimes: elastic, plastic, and plastic were examined, with emphasis given to the elastic and the early part of the plastic regime, where differences in the load/displacement characteristics caused by residual stress were found to have a particularly significant effect. Systematic examination of the relationships among residual stress, contact pressure, and elastic recovery revealed a simple, measurable indentation parameter which correlates well with the residual stress. Using this parameter, an experimental technique is proposed by which residual stresses can be estimated in the elastic/plastic regime with a depth sensing indentation load and depth, the yield stress, and the elastic modulus of the material, all of which can be determined by load and depth sensing indentation methods. Based on an critical examination of the technique by finite element simulation, the technique appears promising.

Spherical indentation with load and depth sensing is a useful technique for characterizing thin film mechanical properties. With this technique, the initial loading is in the elastic range. Therefore the elastic-plastic transition can be observed. However, the calibration of spherical indenters presents special problems. First, the radius of the indenter at the point of contact must be determined, and any deviation from a spherical radius must be evaluated. The shape of the indenter also causes mounting difficulties that can create a relatively large and nonsymmetric indentation in the testing machine. The calibration of spherical indenters is further complicated, because sensitivity to the indenter and surface roughness add to the uncertainty in locating the surface of the sample. In addition, spherical indenters are generally made of single-crystals, and the calculation of their elastic response must include their anisotropy. To address these difficulties, a methodology for the calibration of spherical indenters, whereby indentation experiments are conducted on multiple ceramic materials in the elastic range. The method was used to determine the local radius of a symmetrically spherical indenter. The accuracy of this measurement was verified using confocal microscopy. Using this indenter, the total machine compliance was approximately twice the compliance of the same machine using a diamond Berkovich indenter. In addition, the nonlinearity of the machine compliance was determined. Further results involving indentation in the plastic regime will also be presented.


V4.20 A METHODOLOGY FOR THE CALIBRATION OF SPHERICAL INDENTERS. J. Gregory Swadener, George M. Pharr, University of Tennessee, Dept. of Materials Science and Engineering, Knoxville, TN and Oak Ridge National Laboratory, Metallurgy and Ceramics Division.

Spherical indentation with load and depth sensing is a useful technique for characterizing thin film mechanical properties. With this technique, the initial loading is in the elastic range. Therefore the elastic-plastic transition can be observed. However, the calibration of spherical indenters presents special problems. First, the radius of the indenter at the point of contact must be determined, and any deviation from a spherical radius must be evaluated. The shape of the indenter also causes mounting difficulties that can create a relatively large and nonsymmetric indentation in the testing machine. The calibration of spherical indenters is further complicated, because sensitivity to the indenter and surface roughness add to the uncertainty in locating the surface of the sample. In addition, spherical indenters are generally made of single-crystals, and the calculation of their elastic response must include their anisotropy. To address these difficulties, a methodology for the calibration of spherical indenters, whereby indentation experiments are conducted on multiple ceramic materials in the elastic range. The method was used to determine the local radius of a symmetrically spherical indenter. The accuracy of this measurement was verified using confocal microscopy. Using this indenter, the total machine compliance was approximately twice the compliance of the same machine using a diamond Berkovich indenter. In addition, the nonlinearity of the machine compliance was determined. Further results involving indentation in the plastic regime will also be presented.

Research sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22941 with Lockheed Martin Energy Res. Corp. This research was conducted using the Shared Research Equipment User Facilities at ORNL.


It has been understood for some time that elastic energy can cause surface roughening during a solid surface motion. This instability has recently led to a novel experimental technique to determine stress state on the surface of a solid by measuring the surface profile before and after etching [1]. Along a separate line of investigation, Aziz and co-workers have recently described a different kind of instability, also driven by stress [2]. Their experiments showed that the activation energy of the surface mobility depends linearly on the stress normal to the surface, and this dependence can cause surface instability. The two kinds of instabilities have very different characteristics. In this paper, we describe a linear stability analysis of a three-dimensional interface evolving under stress. The interface can be destabilized either by stress-dependent activation energy or by elastic energy. We discuss the implications of the results for several experiments. [1] K.S. Kim, J.A. Hartland and H. Tan, Evolution of surface roughness spectrum caused by stress in a nanometer-scale chemical etching. Submitted for publication. [2] W. Barovs Carver and M.J. Aziz, L.J. Gray and T. Kuglar, Kinetically driven growth instability in stressed solids. Phys. Rev. Lett. 81, 1445-1448 (1998).

V4.22 IN SITU CHARACTERIZATION OF STRESS DEVELOPMENT IN LOW DIELECTRIC CONSTANT SILICA FILMS DURING DRYING AT LOW TEMPERATURE. Mingching Lu, Qinghai Li, Chul-Soo Kim, and C. Jeffrey Brinker, Advanced Materials Laboratory, Sandia National Laboratories and the University of New Mexico/NSF Center for Micro-Engineering Materials, Albuquerque, NM.

Low dielectric constant silica films are made using ambient temperature and pressure aerogel process or a surfactant (CTAB) templated sol-gel process. This paper will present the in-situ measurement and analysis of stress development during the making of the films, from the onset of drying till the end of heating. The drying stress is measured by a cantilever beam technique; the thermal stress is measured by monitoring the wafer curvature using a laser deflection method. During the course of drying, the aerogel film experiences a biaxial tensile stress due to solidification and initial drying. At the final stage of drying where the drying stress diminishes, dilation of the film creates the porosity of the wet gel state, reducing the residual stress to zero. The surfactant templated films also exhibited drying stress due to the influence of the surfactant on surface tension.
and extent of silicone condensation. Aerogel films develop a large tensile or compressive stress at intermediate temperature (depending on which surface modification regent is used to modify the silicone network) which reduces nearly to zero after further heating followed by cooling to room temperature. For the surfactant templated films, some residual tensile stress remains after the heat treatment is finished. In situ spectroscopic ellipsometry analysis during drying and heating, TGA, DTA, and FTIR are all used to help understand the stress development.

**V.4.23**

**MECHANICAL CHARACTERIZATION OF SURFACES BY NONTRIBOLOGICAL MEASUREMENTS OF SLIDING AND ABRASIVE TERMS.** Samer Issa, Peter Gran, Gunnar Berg, Martin-Luther University, Dept. of Physics, Halle, GERMANY.

In connection with the miniaturization of moving components in many technological devices (computer disk recording systems etc.) the investigation of the frictional behavior of thin films is an important factor, because surface interactions dictate or control the function of practically every device. An elementary way to simulate the multi-disciplinary nature of the tribological behavior of a singleasperity moving against a solid surface is the scratch test with sharp indenters of Vickers or Berkovich type. Here this test is used to investigate the fundamentals of the behavior of the friction of tribological pairs with different mechanical properties in the ultralow load regime. The results show a strong dependence on the normal load and the contact area. This paper presents a new method of data analysis, which allows a full interpretation of the load dependence of the friction and in particular both sliding and wear conditions, respectively. On the basis of these results it becomes possible to estimate the acting forces for which the tribological strain becomes minimal. Particular attention is also focused on the effects of adhesion forces between the moving parts. By taking into consideration various theories about the adhesion of solids an estimation of its influence on nanoscratching tests can also be given.

**SESSION V/5:MM/05 JOINT SESSION**

**THIN FILMS FOR APPLICATIONS IN MEMS**

Chair: Richard Vinci

Wednesday, Morning, December 1, 1999

Room 306 (H)

**8:30 AM V.5.1/MM/0.1**

**WAVER SCALE TESTING OF MEMS STRUCTURAL FILMS.** Brian J. Gally, C. Cameron Abnet, Stuart Brown, Exponent, Inc., Norick, MA.

Binary modulus and residual stress of silicon nitride and polysilicon films on silicon substrates were measured at multiple (discrete) locations across individual wafer surfaces using a versatile budge testing method. An array of 0.5 μm thick silicon-etch silicon-nitride membrane was fabricated across the surface of 100 mm diameter wafers. In-plane dimensions of the membranes were 1 mm square. Some of these wafers were coated with an additional 2 μm thick layer of polysilicon, forming a composite membrane. Material parameters of the films were determined by measuring the deflection of the silicon-nitride and composite membranes under controlled pressure. Pressures from 0 to 30 psi were applied across the membranes while the deflected shapes of the membranes were measured using a white-light interferometer. Numerical analysis of the pressure-deflection behavior of the silicon-nitride and composite membranes enabled the binary modulus and residual stress of the films to be mapped over the wafer surface with a sensitivity of better than ±5%. Results from wafers fabricated at three foundries are presented and compared.

**8:45 AM V.5.2/MM/0.2**

**FATIGUE BEHAVIOR OF THIN SILVER FILMS INVESTIGATED BY DYNAMIC MICROBEAM DEFLECTION.** R. Schwenger, O. Kraft, Max-Planck-Institut f. Metallforschung, and Institut f. Metallkunde, University of Stuttgart, GERMANY.

It is well-known that the mechanical behavior of thin films differs from that of their bulk counterparts. For instance, it has been found both experimentally and by modeling that the flow stress of thin films is much lower than the true hardness, and varies inversely with the film thickness and the grain size. This can be explained by both dimensional and microstructural constraints on dislocation movement, which might also affect the fatigue behavior of thin film materials. In this paper we describe a new method that allows the investigation of high cycle fatigue behavior of materials with small dimensions. In particular, fatigue properties of thin Ag films of varying thicknesses were investigated by dynamic microbeam deflection utilizing a commercial nanoindentation system. Silicon dioxide microbeams were fabricated by conventional integrated circuit techniques and a silver film was sputter-deposited onto the patterned wafer. The microbeams were cyclically deformed and the changes in mechanical behavior monitored. Surface plasmon resonances in beam stiffness were observed during the fatigue experiments. The stiffness decrease was related to damage formation in the thin film, including voids, cracks, and extrusions. Several microscopical techniques were applied to microstructureize the beam specimens. The extrusions appeared as narrow ribbons of squeezed-out material located in the interior of single grains. The height of the extrusions was in the range of the film thickness. Voids were found to extend from the film-substrate interface towards the surface. Based on these observations, we suggest a qualitative explanation of extrusion growth in terms of dislocation glide and annihilation associated with the production of point defects.

**9:00 AM V.5.3/MM/0.3**

**BENDING RESPONSE OF A 100 NANOSECOND THICK FREE STANDING ALUMINUM CANTILEVER BEAM.** M. A. Higginbotham, P. T. A. Siff, Dept. of Mechanical & Industrial Engineering, University of Illinois at Urbana-Champaign, IL.

This study investigates the behavior of a free standing thin metal film under bending loads using a micro-electro-mechanical (MEMS) systems device. A 2.1 micron wide, 11.3 micron long and 100 nanometer thick cantilever beam specimen was fabricated from 99.999% pure evaporated Aluminum. The MEMS device is a comb drive actuator fabricated separately from the specimen. The actuator has a force resolution of 1 nano-Newton and has a probe that can deflect the specimen up to 10 microns by point loading. Two cycles of loading and unloading were carried out. The experiment was observed in situ using an optical microscope and was video taped for data acquisition. Plastic deformation was observed in both the loading cycles. The yield stress estimated from the load displacement profile is 841 MPa which is 49 times higher than the published data for pure bulk Aluminum. To the best of our knowledge, this is the first study to determine the bending test of a 100 nanometer thick free standing film showing a significantly large yield stress compared to its bulk counterpart.

**9:15 AM V.5.4/MM/0.4**

**FILM STRESS INFLUENCE ON THE STRUCTURE OF RF MEMS SWITCHES.** R. Strasser, R. Air Force Research Laboratory, E. O’Keefe, University of Missouri-Rolla, J. D. Lee, M. E. L. Lee, T. Air Force Research Laboratory, W. Patterson, AFD, OH, H. T. Henderson, University of Cincinnati, Dept. of Electrical Engineering, Cincinnati, OH.

The performance of microelectromechanical switches (MEMS) is highly dependent on the switches’ constituent materials. The switch material must be able to provide both structural integrity and high electrical conductivity. Cantilever beams, microbridges, and membranes represent typical MEMS structures used in microwaves/millimeter wave applications. In this study, cantilever and bridge microswitches were fabricated on GaAs substrates using bilayers of titanium/gold and molybdenum/gold. The thickness of the bilayers was fixed at 500 nm and the length of the cantilever and bridge beam was varied from 300 to 1000 μm. The stiffness of the bilayers was measured by using the cantilever and bridge beam as a cantilever. A load of 100 mN was applied to the cantilever and bridge beam. The stress was measured using the deflection of a laser in reflection. A moderate increase in the thickness of the top layer is observed when the stress is applied. The stress was measured by using the deflection of a laser in reflection. A moderate increase in the thickness of the top layer is observed when the stress is applied. The stress was measured by using the deflection of a laser in reflection. A moderate increase in the thickness of the top layer is observed when the stress is applied. The stress was measured by using the deflection of a laser in reflection.
measured stress was compressive (-351 and -579 MPa respectively), and changed from -579 to -186 MPa after heat treatment. Similarly stress for (47 and 25% thick) nitride was compressive (-178 and -590 MPa respectively) which changed from -78 to -429 MPa after heat treatment.

Ts [20 nm] and Pt [170 nm] were sputter deposited on the above oxide and nitride films at 100 °C with [Ts/100/Pt/190 nm] 4 min deposition times to form the detector, where: 570 MPa, which changed to 4.3 x 10^6 MPa after RTA annealing at 700 °C for 60 sec. Stress due to the (Ts/Pt) films, deposited on 90 and 255-nm thick oxide were -576 and -860 MPa respectively. The RTA treatment further changed the stress from -567 to -4.8 x 10^6 MPa and -785 to -4.2 x 10^6 MPa. When (Ts/Pt) films were deposited on a sandwich of (Oxide-215/Nitride-2100 nm) films, the measured stress was -1180 MPa which changed to -4.2 x 10^6 MPa after similar RTA treatment. Sol-gel deposited PTZ thin (50 nm) film on Ta/Pt electrodes created an average 400 MPa stress. Several PZT MEMS static pressure sensors were fabricated using dry etching process. Performance of the sensors was measured by capacitance method, values varied from 423 to 907 pF. The effect of the stress on capacitance values was also studied.

9:45 AM V5.6/MM10.6

THICKNESS EFFECTS ON MICROSTRUCTURE AND TRANSFORMATION BEHAVIOR OF COBALT THIN FILMS

Helko Heesemann, Peter Million2, and Eduard Arzt3; Max-Planck-Institut für Metallforschung and Institut für Metallkunde, Universität Stuttgart, Stuttgart, GERMANY; Institut für Angewandte Physik, ETH Zürich, SWITZERLAND.

Martensitic transformations are important mechanisms with respect to shape memory alloys, which are used, e.g. as thin films in microactuators. In order to understand the influence of film thickness on the martensitic transformation, we study the transformation behavior in cobalt films in comparison with CoNi. Cobalt is particularly useful for this purpose owing to the simple crystallography of its martensitic transformation. The austenite and martensite phases are face centered cubic and hexagonal close packed, respectively, and the habit plane is the close packed planes of both phases. The martensite phase does not contain any internal structure such as twins. Co-films of 0.2 μm to 3.0 μm thickness have been sputter deposited on Si substrates. The films have been characterized by electron backscattered diffraction (EBSD), X-ray diffraction and wafer curvature measurement. Upon ongoing thermocycling, the martensitic transformation is reproducibly found in 3.0 μm thick films. In these films, the microstructure changes during the transformation, and also during isothermal annealing from a strong fiber texture to a ring texture. A stress drop in heating as well as in cooling accompanies the martensitic transformation. Whatever the change in texture, a change occurs in film thickness 0.2 μm. It is concluded that the thickness as critical size parameter strongly affects the mutual interaction of structural evolution and martensitic transformation in thin films.

SESSION V6 POLYMER THIN FILMS

Chair: Edward Shaffer II
Wednesday Morning, December 1, 1999
Room 306 (H)

10:30 AM V6.1

INTERFACIAL ADHESION AT POLYMER/POLYMER INTERFACES CONTAINING FILMERS. Hangsun Lee, Bin Tang, Miriam Rachfalia, and Jonathan Sokolov; NSF-NISEO, Garcia Center for Polymers at Engineered Interfaces, Department of Materials Science & Engineering, State University of New York at Stony Brook, Stony Brook, NY; Byoung-Jeong Kim, Division of Biomedical Materials Engineering, Seoul National University, Suwon, KOREA.

The effect of carbon black and clay filler particles on interfacial adhesion was investigated using the ADCB (asymmetric double cantilever beam) method. PS and PMMA slabs were molded and a layer 100 nm thick of monodispersity PS [50K] or copolymer mixture of graft and block polymer containing varying fractions of carbon black, and clay was spun coated on the surfaces. PS/PS, PS/PMMA, and PMMA/PMMA joint were then made. The Ge (interfacial fracture toughness) values were then measured as a function of carbon black and clay content for various annealing times at T=150°C, and also showed as a function of temperature and time dependence with carbon black and clay. The values show a large decrease with Ge with fillers. These effects are interpretation in terms of surface adsorption of the particle to the filler surface.

10:45 AM V6.2

NANOINDENTATION PROBING OF ENVIRONMENTAL EFFECTS ON POLYMER COATING PROPERTIES. N. Xin, K. B. Yoder, L. E. Siverson, W.W. Gerberich, University of Minnesota, Dept. of Chemical Engineering and Materials Science, Minneapolis, MN.

During and after solidification, coatings shrink due to solvent evaporation, phase transformation, chemical reaction, or a combination thereof. Mechanical properties such as modulus, yield stress and adhesion strength will vary with drying due to changing stress situation. There are several factors which can affect the coating mechanical properties, such as humidity, temperature, etc. Firm understanding of their influence will aid in material selection and process optimization for coating systems. The Hystron TriboScope combines nanoindentation testing and atomic force microscope (AFM) imaging. A humidity-controlled chamber has been recently designed for use in situ study of transient influence on coating properties during drying. Initial experiments have been to study the drying properties of poly (vinyl alcohol) (PVOH) coatings. The wet and fully dried coatings obtained from 2% and 5% PVOH solution were tested under 10%, 50% and 70% relative humidity. Elastic moduli were calculated from unloading stiffness and contact area using nanometer scale penetrations. Viscoelastic moduli and viscosities were extracted from indentation creep tests through a newly developed analytical model. Moduli values obtained from initially wet coatings are close to the literature value after enough drying time. Contrary to expectations, the apparent moduli values for a fully dried coating increase with time. This can be caused by the special swelling behavior of PVOH. The microcrystalline domains formed during drying remain enhancing Young's modulus even after the equilibrium water content values are still high, i.e., 87%. A good correspondence between experimental data and theoretical analysis based upon the stress strain viscoelastic model has been found. The modulus changes from fully dried coatings are lower than that from indentation but are increasing with the time too. The humidity chamber is currently being applied to study the properties of a detergent coating based on PVN with SDS surfactant coated courtesy of Dr. Brunst from Unilever, UK. The addition of SDS causes obvious differences in coating properties under different humidity. A temperature stage has also been incorporated to allow nano-mechanical property measurements over a temperature range of -40 to 150°C. Preliminary results of this instrument will be presented. Initially, two material systems are being investigated: bulk sapphire as a calibration base line and bulk low-density polyethylene (LDPE). The former is used as a gauge of instrument performance, since the nano-mechanical properties of sapphire do not change measurably in the temperature range investigated, while the LDPE should exhibit significant variation in properties with temperature.

11:00 AM V6.3

VISCOELASTIC BEHAVIOR OF POLYMER FILMS DURING SCRATCH TEST: A QUANTITATIVE ANALYSIS. Vincent Jardret, Warren Oliver, MTS, Nano Instruments Innovation Center, Oak Ridge, TN.

Dynamic properties of polymer surfaces affect their ability to withstand abrasive actions. Kinetic conditions, like velocity, penetration depth and shape of the abrasive particles, determine the abrasion mechanisms and the morphology of the abraded surface. Using the scratch technique, along with profilometry measurements across the scratch, we have been able to completely characterize the residual scratch morphology. Pileup deformation and visco-elastic relaxation are key phenomena that characterize the importance of ductility in the scratch resistance of polymer surfaces. Cross profilometry aids in studying the relaxation of the scratch morphology for different time and temperature history after the scratch is made. Effect of scratch velocity, penetration depth and indenter geometry on the contact pressure and friction coefficient estimated during a scratch test can also be analyzed. A good correlation was found between normal indentation and scratch testing in the evolution of the contact pressure with the applied strain rate. This work results in a better understanding of the stresses and the strains applied by an abrasive particle, and especially relates the dynamic mechanical properties of viscous materials, like stress exponent, to their scratch behavior. The method presented can provide for the measurement of dynamic properties of polymer surfaces or thin films under a very large range of strain rates.

11:15 AM V6.4

DEVIATIONS FROM ASSUMED BEHAVIOR, THE METALOGY OF 1 MICRON POLYMER FILMS. C. G. D. and L. M. Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD.

The 0.1 micron film thickness threshold presents the promise of faster clock speeds, larger storage capacity, and more commercial opportunities. Recent experimental results on ultrathin (<0.1 micron) polymer films have shown deviations from the assumed bulk behavior. The majority of these studies have employed static thermometry to measure changes in the film thickness as a function of temperature. Good measures of the bulk glass transition temperature of polyethylene
have been known for at least thirty years. Due to the small sample thickness, traditional techniques used to characterize the glass transition generally are not applicable and more advanced metrology was needed to examine the assumed bulk behavior of the materials. New thinking about how to measure the properties is required. In this presentation, the development of two experimental techniques designed to measure the viscosity of these ultrathin films will be presented. The first of these techniques employs a viscosity sensitive fluorescent probe. The second technique uses thin torsional quartz resonators to measure the complex viscoelastic coefficients. The experimental details, working equations and results for a thickness series of supported and free-standing polystyrene films.


Nano-mechanical properties were determined from the organic matrix of a mollusk hard tissue using a nano-mechanical testing instrument attached to an atomic force microscope (AFM). The inner section of red abalone (Haliotis rufescens) shell (nacre, or mother-of-pearl) has a brick and mortar microarchitecture with pseudo-hexagonal shaped bricks made of aragonite CaCO₃ plates (0.25 micrometers thick and 5 micrometers edge length) surrounded by a thin (5-25 nm thick) proteinaceous organic matrix. In addition to the details of the microstructure, mechanical properties of these biocomposite nanostructures were measured. When cleaned, nanometer-sized indentations between the plates resulted in surfaces covered with a thin (<10 nm) film of the organic matrix material. For the estimation of surface roughness and film thickness, cleaved samples were imaged using AFM at scales approximating cleaned carbon coated areas. Measurements of mechanical properties of films of this thickness are at the limit of the resolution of most testing systems. An AFM equipped with a nanodentation system was used to make indentations in low loads (50 to 200 microNewtons). Direct measurement of the elastic properties of the organic matrix requires penetration depths of only a few nm thickness. With conventional Berkovich nanoindenters, even at the lowest loads, stresses are too large to measure soft film properties without the effect of the underlying hard substrate. Metallic (W) wire, therefore, was electrophoretically etched to various spherically-tip radii (1 to 20 micrometers) for use as broader indenters to optimize stress resolution and increase contact area for better sampling. Load-displacement (F-d) curves at low loads (50 and 100 microNewtons) revealed almost entirely elastic response with an estimated modulus value of about 5 GPa. We will discuss a model for the layered nanostructure behavior by combining the values of elastic moduli from both the organic and inorganic components of the biomimetic structure.

11:45 AM V6.6 MECHANICAL PROPERTIES AND TOUGHENING OF POLYSILSESQUIXANES NETWORKS. Binhong Zhu, Dimitris E. Kassoulis, John R. Keryk, Central R&D, Dow Corning Corporation, Midland, MI; Frederick J. McGrady, Department of Materials Science and Engineering, M.I.T., Cambridge, MA.

Polysilsesquioxanes are used as interlayer insulting materials for microelectronics. However these materials are brittle, especially under tension caused by the thermal expansion mismatch and cracking shrinkage. In this study the mechanical properties of several representative cured polysilsesquioxanes networks are studied and some toughening approaches are demonstrated. The mechanical properties of these networks strongly depend on curing conditions. After a relatively low temperature cure the room temperature fracture toughness of the networks is controlled by the damping capability of the network, while such damping mechanisms play a less important role after a high temperature cure. Different toughening approaches can be designed for each region according to applications. The Phase I and Phase I/II toughening approaches, involving the incorporation of polydimethylsiloxane chains of different lengths, effectively increase the fracture toughness of the networks.

SESSION V7/110 JOINT SESSION:
MECHANICAL PROPERTIES OF AMORPHOUS AND CRYSTALLINE CARBON
Chairs: John Robertson and Edward Shaffer II
Wednesday Afternoon: December 1, 1999
Room 311 (H)

1:30 PM *V7.1/U10.1 TRIBO-CHEMISTRY OF ZDOL DECOMPOSITION WITH HYDROGENATED CARBON OVERCOATS. C. Singh Bhatia, IBM, San Jose, CA; Chao-Yuan Chen; Walter Fong; Changsheng Jing; Donald B. Bogy, University of California, Department of Mechanical Engineering, Berkeley, CA; Simone Anders, Lawrence Berkeley National Laboratory, Berkeley, CA.

Tribo-chemical studies of the lubricant molecular weight effect on the tribology of the head/disk interface (HDI) were conducted using hydrocarbon (CH₄) disk coatings with ZDOL lubricant. The studies involved drag tests with uncured and carbon-coated AlOx/Ti metalized sputtering TiAlOx/Ti sputtering description experiments in an ultra-high vacuum (UHV) tribochamber. The studies showed that the lubricant interaction with the carbon overcoat varies as a function of lubricant molecular weight. The friction coefficient increases as the molecular weight increases. The higher friction is due to the higher viscosity. The friction and catalytic decomposition mechanisms of ZDOL are described. In general, the PFPE polymers are decomposed by chain scission involving the breakdown of the backbone bonds to yield free radical segments which are susceptible to chain scission by the free mechanisms: (1) random degradation, (2) depolymerization, and (3) weak-link degradation. Our studies further support previous observations that catalytic reactions occurred at the endrup functional group. The lower number of endrup functional group for ZDOL with higher molecular weight reduces the possibility of the occurrence of catalytic reactions. Moreover, the ZDOL described peak temperatures shifted to lower temperatures with increasing molecular weight in thermal desorption tests. The spreading diffusion coefficient of ZDOL decreases with increasing molecular weight. As the mobility of the lubricant chains decreases, the diffusion energy needed to break the lubricant chains increases, resulting in higher description peak temperatures. In addition, the fragility chain length of the higher molecular mass ZDOL causes higher degrees of crosslinking. The crosslinking restricts chain conformation and causes a decrease in the description peak temperatures. In summary, the work will discuss the lubrication effect due to tribo-chemical reactions at the head/disk interface.

2:00 PM V7.2/U10.2 IN-SITU WEAR MEASUREMENTS OF THIN CARBON FILMS. Paul Novotny, Terracon Corporation, San Jose, CA; Boris Drez, Veeco Instruments, Inc., Plainview, NY.

First optical surface recording heads and disks represent an ideal system to study tribology in thin films in-situ with high sensitivity. Quantitative measurements of wear of thin films usually involve an ex-situ evaluation of wear with mechanical profilometry, atomic force microscopy, optical interferometry, ellipsometry or flying height interferometry. The optical beam that passes through the head can be used to monitor the head-disk spacing and, therefore, the wear of the thin film coated on the head surface. When the disk contains tracking grooves, diffraction of light from lands and grooves produces a tracking error signal, which depends on head-disk spacing. In addition, the light coupling between the head and disk optical surfaces generates an optical coupling signal that also depends on head-disk spacing. Moreover, an acoustic emission sensor produces signals, which monitors physical contacts between surfaces on the head and disk and effectively measures physical head-disk spacing. Head-disk spacing is adjusted externally, and tracking, coupling and acoustic signals are calibrated as a function of optical or physical head-disk spacing. When a wear test is carried out, time series of these signals with time provides a direct measure of the remaining film thickness or the local wear rate. The thin film wear rate is followed in situ with the above techniques and the final amount of wear is measured with ex-situ techniques. These new tribology techniques have been applied to comparison of the wear rates of thin ion beam and cathodic arc carbon films. The elastic modulus and machinability of these films were 150 and 250 GPa, and 25 and 55 GPa for ion beam and cathodic arc films, respectively. An adequate agreement was obtained between in situ and ex-situ measurements with film thickness resolution down to 1 nm and spatial resolution down to 200 nm. Cathodic arc carbon films showed significantly lower wear rates than ion beam deposited carbon films.

2:15 PM V7.3/U10.3 MICRO-WEAR SCAN TEST ON THE CARBON OVERCOATS A THIN AS C6M ORLIES. T. W. Wu, IBM Almaden Research Center, San Jose, CA; T. W. Schurp, The University of Alabama, Center for Materials for Information Technology and the Department of Metallurgical and Materials Engineering, Tuscaloosa, AL; Hong Zhang, IBM Storage Systems Division, San Jose, CA.

The integrated mechanical strengths and failure mechanisms of ultrathin nitrogen-doped carbon overcoats (CNAs) have been assessed by micro-wear scan technique. These thin coatings, with a thickness ranging from 1 to 6nm, were deposited on magnetic recording disks by a DC-sputtering process. In the course of a micro-wear scan, while the indenter is oscillating along the x-direction at a frequency of 2Hz to perform the wear function, the tip scans at a
speed of 0.18 um/second along the x-direction with a gradually increased load. Because of this reciprocating, ramped-loading and scanning combined test scheme, the micro-wear scan has a unique advantage to create a continuous wear track and preserve the wear morphology inside. Furthermore, a wear track of 20um by ~85um in size facilitates many surface analyses, such as high-resolution SEM and AES. A critical load, defined as the first occurrence of contact damage, was used as a semi-quantitative measure of the mechanical strength of these overcoats. It was found that the critical load decreased in a nearly linear manner with the CNx thickness down to the ~20nm regime. However, the sharp decrease in the thick CNx trend and its critical load decreased dramatically. High-resolution SEM was employed to reveal the details of the micro-wear pattern and the CNx failure mechanism will be illustrated and discussed.

2:30 PM V7.4/U10.4 ELASTIC CONSTANTS OF DIAMOND-LIKE CARBON FILMS BY SURFACE BRILLOUIN SCATTERING. A.C. Ferrari, J. Robertson, Engineering Dept, Cambridge University, U.K.; P. Grassi, M. Beghi, C.E. Borrelli, Dip di Ingegneria Nucleare, Politecnico di Milano, ITALY.

The determination of the elastic constants of thin, as-deposited films is extremely difficult. The reduced Youngs modulus is often extracted as from nanoindentation tests used to measure hardness. Laser-induced surface acoustic waves (SAWs) can also be used. The difficulties of using nanoindentation for hard thin films on softer substrates, such as tetrahedral amorphous carbon on Si, are well known. Whilst the hardness values derived by indentation for tCN are found to be between 60 and 80 GPa, however, the Youngs modulus values derived by indentation are considerably more widely scattered. It has been found that Surface Brillouin Scattering (SBS), a SAW method, can be used to determine the first four elastic constants of hard-on-hard films, even those less than 1nm in thickness [1]. We find that the Youngs modulus and Poissons ratio of tCN with an 88\% sp3 fraction and 3.25 GPa/cm^3 density are 755 GPa, 337 GPa and about 0.12 respectively. We find for tCN with 70\% sp3 and 3.05 GPa/cm^3 density these values are 300 GPa, 115 GPa and about 0.3. The data help to resolve the previous uncertainties in mechanical data. They show that the Youngs modulus for tCN is less than diamond, while the modulus of tCN is considerably less than that of tCN because of the weakening effect of C-H bonding.


A computer-controlled Nanoindentor was used to test amorphous diamond samples in uniaxial tension by pulling linearly at a frst tipped diamond. Two sample designs were attempted. The first design was a single-layer specimen where one end was rigidly attached to the substrate and the opposite end was glued to the tip of the Nanoindentor. The second design was of two layers to permit the construction of samples with freely moving pivots at the fixed end. Tensile load is calculated by resolving the measured lateral and normal forces. Hardness and fracture toughness were determined by numerical methods. Displacement is corrected for machine compliance using the differential stiffness method. Post-mortem examination of the samples was performed to document the failure mode. The yield and ultimate strength derived from these measurements are in good agreement with the data presented in the text. The strength of these samples is consistent with a 50\% sp3 fraction.

3:30 PM V7.6/U10.6 USING FINITE ELEMENT MODELING TO UNDERSTAND THE EFFECTS OF INDENTER SHARPNESS ON HARDNESS MEASUREMENTS OF THIN DLC FILMS ON SI SUBSTRATES. P.J. Wolff, E.G. Herbert, and B.N. Lucente, MTS Systems Corporation, Nano Instruments Innovation Center, Oak Ridge, TN.

The use of thin DLC films as mechanically protective overcoats is common in many aspects of the magnetic recording media industry. One technique that has been widely used to quantify the mechanical properties, specifically the hardness, of these films is depth-sensing indentation. However, it is well known that as the thickness of the film decreases, the ability to quantitatively determine properties from analytical techniques becomes increasingly difficult. This paper examines, from an experimental and FEM approach, the effect of indenter tip sharpness on the ability to accurately determine properties of 20 nm DLC films on Si substrates, a common industry configuration for testing. Experimental results for indenters with varying tip radii obtained using current analytical models will be compared to FEM calculations performed using indenters of the same, rectangular geometry. The evolution of the hardness under the indenter is presented in an effort to more clearly explain the measured results.

3:45 PM V7.7/U10.7 MICROCRYSTALLINE AND NANOCRYSTALLINE DIAMOND FILM DEPOSITION ON COBALT CHROME ALLOY. Marc D. Fris, Yogesh K. Vohra, Univ of Alabama-Birmingham, Birmingham, AL.

Medical implants ranging from tooth replacement posts to artificial hips, knees, and shoulders are commonly constructed of cobalt chrome alloy. These artificial joint components, in particular, are highly sensitive to wear and are usually replaced after ten years of use. In order to extend these implants' service lifetimes, a thin film of diamond will be applied to the implant's surface by microwave plasma chemical vapor deposition (MPCVD) following MPCVD nitridation. Cobalt chrome often deforms uniformly during deposition due to a high thermal expansion mismatch of 13.5 K^-1 for cobalt chrome as opposed to only 1.35 K^-1 for diamond. Additionally, cobalt chrome promotes the degradation of the growing diamond film into graphite, by absorption of carbon into the metallic lattice. By nitriding the cobalt chrome through MPCVD prior to diamond deposition, a usable diamond film may be achieved. Since both nitriding and deposition will be performed by MPCVD, there is the possibility of merging the nitriding and deposition steps into one growth process. We will also present experimental data on microcrystalline deposition as well as nitrogen-nitrided nanocrystalline deposition. Residual stress will be analyzed through Raman laser spectroscopy and thin film X-ray diffraction (XRD).

Research supported by NASA EPSCoR and Alabama Space Grant Consortium.

4:00 PM V7.8/U10.8 FABRICATION AND CHARACTERIZATION OF FUNCTIONALLY GRADIENT DIAMONDLIKE COATINGS. Q. Wu, A.K. Sharma, S. Yarmolchko, J. Smucker and J. Nyangan, NSF Center for Advanced Materials and Smart Structures, 1 Dept of Mechanical Engineering, McNair Hall, North Carolina A&T State University, Greensboro, NC, 2Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Pure diamond-like thin films thinly layered by four-fold coordination suffer from a large internal compressive stress that gives rise to serious adhesion problem. In this work, functionally gradient diamond-like thin coatings were prepared by pulsed laser deposition in a high vacuum as an alternative approach to address the adhesion problem of diamond-like films. Copper, silver and titanium were incorporated into the growing films with their concentration as a function of distance from the substrate surface. The top of the thin coatings is pure DLC of about 200nm in thickness. We will also present mechanical characterizations using Nanoindentor XP™ were carried out to study the mechanical behavior of the functionally gradient DLC films. Scratch tests were made to assess the improvement in adhesion.

4:15 PM V7.9/U10.9 NANOMECHANICAL PROPERTIES OF AMORPHOUS CARBON AND CARBON NITRIDE THIN FILMS PREPARED BY SIMPLIFIED ARCION PLASMA. Nobuhiko Makino, Yoshikazu Hiyoshi, Iwakuni Sugiwara and Osamu Takayama, Department of Materials Processing Engineering, Graduate School of Engineering, Nagoya University, Nagoya, JAPAN.

Hydrogen free amorphous carbon (a-C) and carbon nitride (a-CN) were synthesized by dehydrogenated arc ion plating in which a sheeting plate was inserted between a target and a substrate in order to prevent amorphous micro-particle deposition on the substrate. The films of a-C and a-CN were prepared in an arc discharge plasma of argon or nitrogen gas, respectively, at a pressure of 1 Pa using a graphite target as anode. Mechanical properties of these films were studied in relation to substrate bias voltage with a nanoindentor. The a-C film prepared at a bias of -100 V consisted of diamond-like phase and showed a maximum hardness of 35 GPa, whereas the film deposited at a bias of -500 V had a minimum hardness of 7 GPa indicating that the film was converted to be graphite-like due to excessive ion impact in the Ar plasma. The wear resistance of the a-C films depended on the hardness, namely, harder a-C films were more wear resistant. On the contrary, the hardness of the a-CN films, which remained in the range of 10 to 14 GPa, was less dependent on the bias voltage and much lower than the maximum hardness of the a-C films. Nevertheless, the wear resistance of the a-CN films was comparable to or better than the a-C films. In particular, the a-CN film prepared at a bias of -300 V was wear resistant that this film converted to graphite-like due to excessive ion impact on the substrate and showed a minimum hardness of 14 GPa.

**4:30 PM V7.10/U10.10**

**INTRINSIC STRESS MEASUREMENTS IN CVD DIAMOND FILMS.** J. G. Kim, Hyundai Electronics Ltd., Icheon, Korea; Jin Yu and Y. C. Kang, Dept. of Materials Science and Engineering, Thejon, Korea.

Diamond films were grown over the (100) Si substrate by the hot filament technique. CVD diamond films were grown using the CH$_4$/H$_2$ gas mixture with varying CH$_4$ content, and the substrate curvatures were measured ex situ at various stages of the film growth. In order to measure the intrinsic stress in the film, substrate curvatures originating from the substrate creep and the thermal stress associated with the ex situ measurements were carefully taken into account. Creep deformation of the Si substrate due to the thin film stress at the curent temperature was measured after removing the diamond layer using the reactive ion etching method. Results showed that the intrinsic stress in the film was always positive increasing with the film thickness and decreasing with the CH$_4$ content, and that a failure to consider creep of the substrate would overestimate the film stress by more than a factor of two. Later an elastic/plastic analysis was conducted to calculate the creep strain and deduce the intrinsic stress without tedious diamond etching process. The method involved analysis of the bend creep and showed reasonable agreement with the experiment. Finally, in order to understand the origin of the intrinsic stress in the diamond film, an analysis based on the density and grain size measurements of diamond films showed that intrinsic stress evolved mainly out of the grain growth during the film thickening.

**4:45 PM V7.11/U10.11**

**REDUCING INTRINSIC STRESS BY CONTROLLING GRAIN BOUNDARY FORMATION.** Brian W. Sheldon, Ashok Rajamani, Janet Franks, and Thomas L. Sklad, Division of Engineering, Providence, RI; Barbara L. Walden, Trinity College, Physics Department, Hartford, CT.

The primary objective of this research is a better understanding of the relationships between intrinsic stress and grain boundary formation. This work involved experiments with several different materials, including CVD diamond and epitaxial nitride. In all of these cases, significant tensile stress evolves during island coalescence, and large reductions in this intrinsic stress were obtained by controlling the coalescence process. In particular, changes in the deposition chemistry during coalescence can have a significant effect on the resultant intrinsic stress. Stress was monitored by using bending plate curvature measurements, and films were also characterized with electron microscopy, Raman spectroscopy, and x-ray diffraction. In addition to the experimental results, mathematical models have been created to describe how the film structure evolves. These efforts demonstrate that stress evolution during island coalescence can be strongly affected by different kinetic mechanisms and by island morphology.

**SESSION V8. ADHESION AND FRACTURE**

Chair: Jerrold A. Floro and Thomas J. Wyrobek

**4:45 PM V8.10**

**THE BRITTLE TO DUCTILE TRANSITION (B/D) IN ADHERED THIN FILMS.** William W. Gerberich, A. Volinsky, N. Tymink, Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN; and N.R. Moody, Sandia National Labs, Livermore, CA.

It has been long recognized that the B/D transition in bulk materials may be associated with enhanced plastic energy dissipation. This can be achieved by either increasing the state of stress (axial strain or plane stress) or by raising the test temperature (lowering the yield stress). The situation is somewhat different in thin films where the B/D transition can be achieved by increasing film thickness or, possibly, even in a limited temperature range, by raising the test temperature. To study the later we use a superhysteretic technique with a 1 μm tungsten film on top of thin copper films bonded to SiO$_2$/Si wafers. This involves indenting into the superhysteretic which stores and then releases large amounts of plastic energy into the thin film/substrate interface. Here, preliminary data on 500 nm thick Cu demonstrates more than an order of magnitude increase in fracture energy from about 10 to 200 J/m$^2$ as the test temperature is raised from 20°C to 130°C. As the amount of plastic energy dissipation is limited by film thickness, this relatively large value was unexpected. This interfacial fracture energy translates to a stress intensity of 5 MPa m$^{1/2}$. In context of the highest possible nanocrystalline Cu yield strength, this still represents a plastic zone of about 4 μm. This illustrates the quandary associated with explaining such high apparent toughness values as one generally expects plasticity to be truncated by film thickness. In this association with:

- some artifact of assessing local stresses during nanoindentation at elevated temperature;
- extending the plastic zone in the direction of crack growth further than the film thickness;
- shielding mechanism from an organized dislocation array in a ductile film sandwiched between a brittle substrate and a higher yield strength superlayer;
- some plastic energy dissipation in the superlayer;
- or by enhanced mode II at higher temperatures? A few of these will be addressed in some detail with a goal of narrowing the field of the most promising candidates.

**9:00 AM V8.2**

**MODIFIED EDGE LIFTOFF TEST: EXPERIMENTAL MODIFICATIONS FOR MULTILayer SYSTEMS.** Eric Langer, Xino Hu Liu, Jack C. Hsu, IBM Research, Yorktown Heights, NY.

One critical parameter affecting the manufacturing and long-term reliability of microelectronic devices is the strength of interfaces. Originally developed for the characterization of a polymer on a rigid substrate, the modified-edge-liftoff test (MELT) is frequently used in the microelectronics industry for the characterization of energy release rates of critical film systems. The strain energy available for driving the interfacial crack is derived from an epoxy superlayer which has a thermal expansion coefficient which is much greater than that of the silicon substrate. In addition to the necessary mechanics modifications, experimental modifications to the test are described for applications of the technique to multi-layer systems. Observations suggest that the largest starter flaws typically occur at the interface between the silicon substrate and the first film layer, due to dicing. These flaws often run in the interface between the silicon, the first film layer, and not the interface of interest. For some systems, it is possible to use creative sample preparation techniques to produce a large starter flaw at the interface of interest. Data suggests that a two-step preparation method yields clean delaminations at the interface of interest. First, the edges of the test coupon are polished to a mirror finish, removing any dicing flaws in the silicon. In the case of a metal/dielectric interface, wet etching is then used to etch the metal, creating a large starter flaw on the desired interface.

**9:15 AM V8.3**

**MICROMECHANICS-BASED MODELING OF INTERFACIAL DEBONDING IN MULTILAYER STRUCTURES.** Patrick Klein, Sandia National Laboratories, Livermore, CA; Huanjun Gao, Ann Vainio, Stanford University, CA; Harry Fujimoto, Qing Ma, Jin Lee, Intel Corporation, Santa Clara, CA.

Classical approaches to modeling fracture have proved successful in applications for which the highly deformed near tip region is small compared to any other relevant dimensions in a structure. The classical theory relies on phenomenological criteria for material failure that lack a physics-based description of the fracture process itself. Small scale, thin film structures pose difficulties for analysis by these approaches because they contain many geometric and microstructural features within the fracture process zone itself. Moreover, plastic flow in metal layers is often severely constrained by the surrounding interface, causing the plastic dissipation part of the overall fracture energy consumed by debonding to be a strong function of geometry. Therefore, the fracture toughness becomes length scale dependent and can no longer be regarded as an intrinsic material property. To improve the fracture characterization of these structures, one must develop a physically sound methodology capable of separating the contribution of plastic flow, and other sources of dissipation, from the work of adhesion consumed at the crack tip. In this study, we investigated the parameters affecting energy dissipation by interfacial debonding in a multilayered structure possessing both stiff, elastic layers and layers exhibiting plastic flow. Interlayer decohesion is modeled by two methods: a cohesive surface formulation and the Virtual Internal Bond constitutive model. Though the parameters of each model may be selected to reproduce the slip work of adhesion and cohesive strength, the stress distributions they produce in the process differ. These differences raise the question of how many parameters are sufficient to characterize the cohesive nature of a multilayer interface. We compare the predicted interaction and the macroscopic fracture energy with experimental results for varying layer geometry. We also characterize the effect of variations in material properties and other experimental uncertainties in the resulting debonding behavior.

**9:30 AM V8.4**

**ANALYSIS OF ADHESION STRENGTH OF INTERFACES BETWEEN THIN FILMS USING MOLECULAR DYNAMICS TECHNIQUE.** Tomio Iwasaki, Hideo Murak, Mechanical Engineering Research Laboratory, Tokyo, Ltd., Tsukuba, Japan.
Advanced Micro Devices, Sunnyvale, CA.

A new experimental technique is developed to measure the fracture toughness of a hard nickel phosphide (NiP) thin film deposited on a soft aluminum substrate. A pre-crack was fabricated in the thin film by using the advanced focused ion beam (FIB) milling technique. The crack extension force was measured using the MTS micro indentation testing with the crack tip opening displacement model (CTOD), the fracture toughness of the thin film was calculated. The results show that the NiP thin film fracture toughness is ~15MPa m^{1/2}.

11:00 AM V8.8
ON THE ROBUSTNESS OF SCRATCH TESTING FOR THIN FILMS: THE ISSUE OF TIP GEOMETRY FOR CRITICAL LOAD MEASUREMENT. Vincent Jachiet, Warren Oliver, MTS Nano Instruments Innovation Center, Oak Ridge, TN.

Scratch and abrasion resistance of hard protective thin films and polymer coatings is often related to their ability to withstand abrasive conditions without fracturing. Wear particles generate catastrophic and severe wear for hard films, and fractured scratches are often very visible on shiny polymer surfaces. Using a particular abrasive particle size and the fracture resistance of the surface can be characterized by the load required to create friction damage. The scratch technique has demonstrated its ability to create these damage mechanisms and characterize the critical load for coatings failure. This technique does not yet have the reproducibility and robustness required to be implemented in an industrial environment. The major reason for this lack of robustness is the great influence of the indenter geometry on critical load results and the non-reproducibility of the geometry of conical indenters. This paper addresses this issue and presents a fast and robust method to characterize the indenter geometry based on the indentation technique. Indenters with radii smaller than micron were chosen to characterize thin films of different nature and thickness. The influence of tip geometry on the critical load results is presented for paint coatings and hard protective thin films. The reproducibility of the critical load measurement using different indenter tips of identical geometry, as shown in this paper, represents a considerable technological breakthrough in abrasion testing and demonstrates the scratch tests ability to control the manufacturing quality of thin films in an industrial environment.

11:15 AM V8.9
MECHANICAL BEHAVIOR OF INDUML OXIDE THIN FILMS ON POLYMER SUBSTRATES. D.R. Chinn, S.M. Schimmin, D. Spearing, R. West, G.C. Paine, Brown University, Division of Engineering, Providence, RI.

The integration of ceramic thin films of thin doped indium oxide – a transparent conductor – with mechanically dissimilar polymer substrates is an essential step in the development of lightweight flexible panel display systems. One widely touted application is the wearable flexible flat panel display but such devices will require materials systems that are mechanically dissimilar with respect to adhesion, kinking, and point loading all which result in large inhomogeneous local strains. We have investigated the mechanical behavior and electrical failure of Sn-doped indium oxide deposited on a variety of polymer substrates (polyethylene terephthalate, acrylic, plexiglass) materials loaded in uniaxial tension while monitoring the evolution of the thin film microstructure using in situ resistivity measurements and ex situ AFM and electron microscopy. In one study we have modeled the evolution of cracking in ITO in films ranging from 10 to 200 nm in thickness on 150 micron thick PET substrates. We show that although failure occurs via the intergranular propagation of micro cracks these crack do not tend to propagate across the gauge length of the specimen, a crack pattern is observed that allows strains in excess of 5% to be measured before catastrophic failure (arbitrarily defined as a 10% increase in resistivity) of ITO on PET when loaded in uniaxial tension. Furthermore, we have established that the fracture origin unit cell of the film can be combined with the need to minimize the temperature seen by the polymer substrate means that thinner films tend to be amoraphic (as established by GIAXD). The interplay of these observations with the mechanical properties of the indium oxide on polymer interfaces is still in process.
SESSION V9: RELIABILITY IN MICROELECTRONICS
Chairs: Karen Meez and Ralph Spolenek
Thursday afternoon, December 2, 1999  Room 306 [H]
1:30 PM V9.1  STRESS DEVELOPMENT IN DIELECTRIC THIN FILMS
Robert E. Cook, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN.

The development of thin films or multilayer structures with advanced electrical properties is frequently impeded by a lack of mechanical reliability or stability of the films or structures. This is particularly so for low dielectric-constant films formed by the liquid-applied coating of a semiconductor wafer substrate followed by solidification of the film during curing. In many films, the high-temperature curing process generates tension in the film through (i) the reaction-solidification process at the curing temperature and (ii) a positive thermal expansion mismatch with the substrate on cooling from the curing temperature. Adherence of the film to the substrate constrains the strain mismatches that would otherwise develop, leading to residual tensile stresses, which in turn can lead to film cracking and delamination. Here the development of mechanical properties during curing of low-temperature spin-on glass materials is considered, with particular emphasis on the development of the thermal and thermal stresses. Spin-on glasses are candidates for use as low dielectric-constant insulating materials in advanced microelectronics for different application structures where great mechanical reliability is required during fabrication and in use. Attention is focused on the effects of residual stresses on stress-corrosion cracking of spin-on glasses.

1:20 PM V9.2  ADSORPTION/DESORPTION PHENOMENA IN SILICATE GLASSES: MODELING & APPLICATION TO A SUB-MICRON BI-CMOS TECHNOLOGY
Thomas Hoffman, Vincent Senez

ISEN-IEMN, UMR CNRS8520, Dept. of Process Simulation, Villeurbanne d’Aix, FRANCE; Philippe Le Dée, Philips-Components, Thin Films & Back-End Engineering, Chenn, FRANCE.

Most of the materials used in modern integrated circuit processes may undergo structural evolutions after deposition (i.e., residual stress and thickness variations) following upon further temperature change or interactions with the ambient. Borophosphosilicate glass (BPSG) films and phosphosilicate glass (PSG) films are widely applied as dielectric layers in VLSI circuits because doped oxides can be reflooded at relatively low temperature to planarize the circuit topology. However, the moisture resistance of highly doped oxides is reduced compared to thermal or undoped oxides and may determine the electrical properties of the devices. Consequently, it is valuable to correlate the water concentration and the corresponding mechanical stress, since the direct measurement of the water contained in films is tricky compared to the residual stress. This paper presents a numerical model implemented in our two-dimensional Finite-Element process simulator IMPACT-2, allowing the evaluation of the mechanical stresses generated by deposited oxides in case of adsorbing or desorbing of water. The algorithm calculates successively the water diffusion in the exposed films and then the mechanical strain/stresses corresponding to the film volume increase (adsorption) or shrinkage (desorption). Experimental measurements giving the variation of stress in doped [PSG, BPSG] and undoped silica glasses over long storage periods provide the data to calibrate the diffusivity of water into these films, at room temperature. Then, using an in-situ stress measurement technique that measures stress as a function of temperature, large hysteresis observed for doped CVD oxides help to calibrate the temperature dependence of the diffusivity. Finally, an extension of this model to simulate the densification of Spin-On Glass (SOG) will be demonstrated. A failure analysis of a recent BiCMOS industrial process will validate the capability of the model to evaluate and minimize the risk of crackings in SOG films during densification.

2:15 PM V9.3  MOLECULAR MECHANICS STUDY OF SURFACE STRESS IN SILICON OXIDE LAYER
Aruba Yamada, Seichi Tomari, Akira Endou, Kunio Terasaki, Moomi Kubo, Akira Miyamoto, Tokuko Univ., Dept. of Materials Chemistry, Sendu, JAPAN; Akiko N. Ichikawa and Masahito Kijjima, National Research Institute for Metals, Tsukuba, JAPAN.

Due to the technological importance of silicon integrated circuit, the oxidation of silicon surface has received considerable attention. Low-temperature processing of semiconductors is of interest because the thermally activated defect production and redistribution of impurities are greatly suppressed. Also thermal stresses in the oxides occurring at the high-temperature processing cause a degradation of reliability of the metal-oxide-semiconductor (MOS) devices. Recently Ichikawa et al. reported the real-time observation of the stress change of Si(100) surface during plasma oxidation with applying positive and negative sample biases. They reported compressive and tensile stresses appeared over again in a positive bias applying [1]. In this study, we calculated silicon oxide films using a molecular mechanics (MM) model and the calculated results have been compared with experimental data [1]. MM calculations based on the universal force field potential [2] were performed using the Cerius2 program [3] of MSI. We used a two dimensional periodic slab model for silicon (100) oxide layers. To enable the compressive and tensile stress of surface to occur, only a single thickness of the supercell is fixed. In this model, the oxidation was assumed to be a layer-by-layer model. We made (100) clean surface to 5 thin oxides layers and calculated the optimized structures. In this study, we are proposing the oxide-bridged structure at the tensile stress of positive bias plasma oxidation. Following this step, the compressive and tensile stress are observed in these calculations. These theoretical calculations correspond well to the experimental data [1].


2:30 PM V9.4  THE MECHANICAL PROPERTIES OF COMMON INTERLEVEL DIELECTRIC FILMS AND THEIR INFLUENCES ON ALUMINUM INTERNCONNECT RELIABILITY
Fei Chen, Baozhen Li, Timothy D. Sullivan, Chun Gonzalez, ChristophD. Muzyj, H.K. Lee, Mark D. Levy, IBM Microelectronics Division, Essex Junction, VT; Michael W. Dushell, James Kolodzey, Electrical and Computer Engineering, University of Delaware, Newark, DE.

Knowledge of the mechanical properties of interlevel dielectric films and their impact on sub-micron interconnect reliability is becoming more and more important as the critical dimensions are scaled down.
For example, the lateral aluminum (Al) extrusions into spaces between metal lines, which become a more of a concern as the pitches shrink, cause Al-Cu intermetallic stress, and stress evolution in conventional and damascene fabrication methods as a replacement. Damascene methods have been shown to be via manufacturing processes for fabricating both Al and Cu interconnects, and the mechanical stress and stress evolution in conventionally-fabricated interconnects has been well documented, mechanical stress generation and microstructure evolution in interconnect lines fabricated using damascene methods has yet to be completely characterized. In fact, recent stress measurements in damascene Cu lines have suggested that the damascene fabrication method may lead to a fundamentally different stress state. In the present work, abbreviated flows from a 0.22 μm technology have been used to fabricate conventional and damascene Al interconnects with similar aspect ratios. The mechanical strain and stress are measured on the product array using X-ray diffraction method. The effect of conventional processing method with the damascene processing method will be shown to influence the strain and stress. In addition the effect of linewidth (from 0.5 μm to 1.6 μm), passivation and thermal history on the strain/stress of damascene Al interconnect lines will be described. While the strain in damascene lines is still the highest in thickness in the CTE, it is strongly influenced by the constraints associated with the fabrication methodology. The implications for reliability will be discussed.

4:15 P.M  **V.9.8**  **PASIVATED INTERCONNECT LINES: THERMO-MECHANICAL ANALYSIS AND CURVATURE MEASUREMENTS**
Adriana Wikstrom, Peter Gudmundson, Dept. of Solid Mechanics, Royal Institute of Technology (KTH), Stockholm, Sweden, Saha Swarup, Dept. of Materials Science and Engineering, MIT, Cambridge, MA.

General equations which are valid for the volume averaged properties of anisotropic passivated lines of arbitrary in-plane shape is formulated. It is shown that additional information is required to solve for the stresses and strains in the lines. The missing information can be expressed (a) theoretically, for certain geometries or (b) by means of additional experimental information such as curvature measurements. Expressions for the average stresses in the lines for the limiting geometries is presented as well as a new method with which the three dimensional volume average stresses can be computed solely from the composite average in-plane stresses obtained from curvature measurements. The method is strictly valid for lines of arbitrary in-plane shape and it requires that certain conditions among the elastic constants in the line and passivation are fulfilled. For isotropic line and passivation materials a simple analytical expression that admits the determination of volume average stresses from curvature measurements is presented. The sensitivity to uncertainty in curvature data is investigated for Si substrates with Al or Cu lines embedded in SOI passivation. It is concluded that the presented approach is well suited for these material configurations.

4:30 P.M  **V.9.9**  **CORRELATION BETWEEN VOIDING AND STRESS RELAXATION IN METAL INTERCONNECTS. Yu-Lin Shen, The Univ. of New Mexico, Dept. of Mechanical Engineering, Albuquerque, NM.

The reliability of thin-film metal interconnects depends strongly on the propensity of voiding. While voiding is a consequence of stress relaxation mechanisms acting on the interconnects, the redistribution of stress will have direct bearing on the subsequent failure processes such as electromigration. We will present our recent analytical studies on the correlation between voiding and stress relaxation. Through computer modeling within the stress relaxation framework, we have quantified how voiding in interconnects relates the thermal stress. Contrary to what many researchers have used in estimating the total anisotropic void volume on the basis of thermal stress, the stress relaxation due to voiding is found to be a local phenomenon, having no direct relation with the global thermomechanical conditions of the device. The short-range nature of stress relaxation is true even when the interfacial sliding between the metal film and dielectric is accounted for in our finite element modeling. The same approach is used to illustrate how the deformed path can induce stress gradient and thus electromigration flux divergence, and to rationalize experimental findings that a pre-existing stress void may or may not grow into an electromigration void. Several common misconceptions regarding voiding, stress evolution and thin-film reliability modeling are also discussed.

4:45 P.M  **V.9.10**  **ELECTROMIGRATION MODELING OF BLEACH EXPERIMENT WITH COMPARISON TO RECENT EXPERIMENTAL DATA.**

Finite element analysis is applied to simulate the electromigration in conventional tungsten junction, which is a typical structure of in Bleach experiment adopted to measure the electromigration drift velocity by edge displacement. Because the specific resistivity of tungsten is...
higher thin that of copper, the electric current crowds at the corner where the underlying tungsten bar connects to the edge of the copper line. This was observed by a silicon detector in other phases of the copper/tungsten interface. Our simulation reveals a stress that may be large enough to crack the interface and is built in in the corner. The evolution of the line resistance under various current densities is measured from our model and compared to the recent experimental results.

SESSION VI.10 POSTER SESSION
Chair: Neville R. Moody and Edward Shaffer II
Thursday Evening, December 2, 1999
8:00 P.M.
Exhibition Hall D (H)

VI.10.1 FINITE ELEMENT ANALYSIS IN DESIGN OF A COATING SYSTEM FOR GLASS FORMING DIES AND TOOLS. D. Zheng, J.J. Moore, Chip垫sunder of Materials Science and Engineering Laboratory, Golden, CO; S. Thiel, J. Diasio, Scott Glass, Mainz, GERMANY.

Development of a high temperature coating system for glass forming dies and tools is required to meet three criteria: non-sticking by molten glass, oxidation resistance, and wear resistance. Inevitably, a functionally multilayered thin film architecture is needed to give an optimized coating for it. Stress-related in a multilayered coating system include intrinsic stresses introduced by film growth process, coherency stresses due to lattice mismatch, and thermal stresses resulting from CTE (coefficient of thermal expansion) mismatch. Finite element analysis has been employed to model the residual stresses and design the architecture of the proposed multilayered coating system. In this FEA, using FEM package MARC, a plane strain model and an axisymmetric model have been developed and a process of X-ray diffraction and electron microscopy between 500°C and 1000°C with a pressing load of 4 MPa has been modeled, in order to determine the optimal thickness of each layer to accommodate and minimize residual stresses in the overall multilayered coating system, and to predict and evaluate the performance and reliability of the coating system for glass molding dies.

VI.10.2 TEM PLANTATION AND MISFIT DISLOCATION FORMATION IN P/P+ SILICON. Petra Freidinger, Hiroko Fukuto, Rajinder Sandhu, Benjamin Post, and Mark S. Goresky, Dept of Materials Science and Engineering, University of California, Los Angeles, CA.

We determined that Si ion implantation (1E14 cm⁻² at 100 keV) of pseudomorphically strained silicon epitaxial layers greatly attenuates strain relaxation. We employed highly boron doped 150 mm diameter silicon wafers with a nominally un-doped, 2 mm thick epitaxial layer (p/p+). The compressively strained layer showed inhomogeneous relaxation after epitaxial growth, with misfits forming only near the wafer surface. This non-uniform dislocation distribution was utilized during the subsequent strain relaxation steps to study the role of the implant on both the nucleation and growth of the misfit segments. The silicon self implantation was performed at room temperature. The dose and energy were kept below the amorphization threshold, as confirmed by triple axis x-ray diffraction and electron microscopy. High temperature rapid thermal annealing was employed to study misfit dislocation nucleation and glide. Double axis x-ray topography was used to measure the evolution of the misfit segments after annealing. The implanted regions exhibited neither growth nor nucleation of misfit dislocation segments, in marked contrast to the growth and nucleation of misfit observed in the non-implanted regions. SIMS measurements confirmed that transient enhanced diffusion of boron was not appreciably different in the two regions, ruling out the reduction of bi-axial stress as the origin for the differences observed. This comparison - and subsequent modeling - indicated that the excess point defects and crystallographic damage act to impede both dislocation motion and dislocation nucleation. Our results suggest that low dose ion implantation has a potential to reduce misfit dislocation propagation and nucleation in multilayer thin films.

VI.10.3 PHOTORELAXATION AND THERMORELAXATION IN GeAsS-AMORPHOUS THIN FILMS. Soukai Aditya-Dina, National Institute for Research and Development, Institute of Microtechnologies, Bucharest, ROUMANIA; Mihai Popescu, National Institute of Materials Physics, Dept. of Materials Science, Bucharest, ROUMANIA.

This work represents a study of the photorelaxation and thermorelaxation in GeAsS₆₋₅₋₀ₓ thin films. X-ray diffraction and microhardness measurements have been performed to characterize these films. The measurements were made on virgin and ultraviolet-irradiated samples, both on as-deposited and annealed films. Experiments were done for the samples with a low Ge concentration (<20%), and a photodarkening effect for the samples with a high Ge concentration (>20%). The two effects have been associated with film softening for x<20 and film hardening for x>20. From the microhardness results it was observed the existence of a topologic phase transition of the GeAsS₂ for x=20, which can be associated with the progressively growing dimensionality in chalcogenide glass (2D to 3D). The results of microhardness measurements and X-ray diffraction spectra have been simulated in the terms of stress relaxation Ge₆₋₅₋ₓAsₓ thin films. The structures remains amorphous, but the characteristic distance of medium range order decreases for x<20 and increases for x>20.

VI.10.4 ESSENTIAL PROPERTIES OF HARD COATINGS FOR LIGHTWEIGHT REDUCED FORMING AND FORGING OPERATIONS. Erich Lugebekker, Otto Kremel, Cyrus Borummi, Kirsten Bohm, Materials Science Institute, Werkstoffwissenschaften, Anchen University of Technology, GERMANY.

In metal cutting the reduction of coolants changes the system tool-workpiece in a wide range. PVD deposited films are to adapt functions of coolants e.g. cooling and lubrication. In interrupted cut machining of tempered steel, for example, the life time of Ta-CN coated inserts is several times greater than the TIN coated ones. This is a result of the favourable thermophysical and tribological properties of Ta-CN. The potential for tool protection of CN is a result of the high hardness and of the low internal stress of this coating material. CN films can be deposited with greater film thicknesses, still maintaining very good adhesion. This paper presents the development of new arc PVD coatings in the system Cr-CN. Due to the high share in the cutting force of the coated tool and a better wear behaviour in comparison to CrN was expected. The effects of various carbon carrier gases on the coating properties were examined. The coating properties were investigated by mechanical tests, X-ray diffraction and SEM analysis. The variation of the aluminium content in TiAlN and the carbon nitrogen ratio in CrCN were compared to the abrasion resistance and the temperature conductivity. Some of the coated were tested in machining tests.

VI.10.5 STRESSES MEASUREMENT AND SIMULATION ON 3C-SiC THIN FILMS. C. Gourley, C. Dalcos, C. Malhure, M. Le Berre, D. Bouvet, L.E. Physique de la Matiere, INSa de Lyon, Villeurbanne, FRANCE; T. Chassagne, P. Abouregni, Y. Mosteil, Lab. Multimateriaux et Interfaces, Villeurbanne, FRANCE.

Although, 3C-SiC has outstanding physical properties to operate in harsh environments the device characteristics and reliability depends strongly on thin films stresses. This paper deals with stress measurements and modelling of 3C-SiC thin films grown on Si or SOI substrates. SiC/Si epitaxy was achieved by plasma enhanced CVD with H₂. The stress measurement by X-ray double crystal Laue and by Raman spectra. The stress by X-ray double crystal Laue was evaluated to be about 25 GPa with a concave curvature of the substrate. The strain by Raman was evaluated to be about 0.3%. The second step was the etching of the substrate with H₂. The silicon substrate was etched away by a mixture of SiC with CH₃SiH₃. Then the third step was the CVD with a SiC ratio of 0.3. Film stress measurements were performed using the bending plate method. The stress for 5 μm thick SiC layer is evaluated to be about 25 GPa with a convex curvature at room temperature. This value is lower than that estimated in earlier works due to an optimization of the deposition process. In addition, measurements at elevated temperature of the substrate curvature were also performed which allows some distinction between thermal and intrinsic stress. Fabrication of epitaxial 3C-SiC free-standing diaphragms by bulk micromachining of the underlying silicon substrate was carried out. Residual stress and biaxial modulus of 3C-SiC films were measured by local deformation measurements using the double crystal Laue diffraction method. The biaxial modulus is compared with the one obtained by nano-indentation. Finally the local deflection measurements of suspended diaphragms are compared with the deflection behavior expected by Finite Element Modelling.

VI.10.6 NHE-Surface Deformation of Painted Polypropylene Blends. Haining Tang, David C. Martin, The University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI.

Quantitative estimates of the interfacial shear strength σ of coatings on substrates are important for a wide variety of technological applications. A tensile mechanical test was used to determine σ between brittle paints and more ductile polypropylene blends. The interfacial shear strength can be derived from measurements of the average crack spacing. Based on a shear lag analysis, the interfacial
shear strength is given by: \( \tau = 3.37 \times 10^3 \sigma_{\text{w}} \), where \( \sigma_{\text{w}} \) is the tensile strength of the paint, \( h_p \) the paint thickness, and \( f \) the average crack spacing. For high-temperature stress generation \( \sigma_{\text{w}} \) in this case is 124 MPa, J. S. J. (1984)]. The influence of simple preparation and tensile strain rate on experimental results has been explored. The near surface deformation was studied by transmission electron microscopy and polarized light optical microscopy. Finite element simulations showed that the stress concentration was related to the difference between moduli of paint and substrate. Micro-indentation experiments were conducted and the results will be compared with those of the tensile mechanical tests.

V10.7 EVALUATION OF MECHANICAL PROPERTIES OF DLC/TiC MULTILAYER COATINGS, R. D. Patel, M. V. Fedoryshyn, Ashok Kumar and M. Shamsuzzoha \* Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL \* Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, AL.

The microaluminate coatings are made of many alternating layers of two hard materials, that, when combined in very thin deposit on the nanometer scale, produce coatings with hardness that approaches diamond. In this report, we address these properties, from our investigations on the multilayer structures of titanium carbide (TiC) and DLC deposited on Si(100) substrates using pulsed laser deposition (PLD) technique. X-ray diffraction and atomic force microscopy were used for the studies of structural and morphological properties of the coatings and the mechanical properties were analysed by the nano-indentation technique. Single layer of TiC and DLC and microaluminate DLC and TiC coatings with varying thickness were deposited on Si(100) substrates. Analysis of mechanical properties revealed that the hardness and modulus of the multilayers are higher to monolithic coatings of either of the two constituent films. The cross-sectional TEM results were analysed to understand the interfacial properties of these microaluminate coatings.

V10.8 DEPOSITION AND CHARACTERIZATION OF MECHANICAL PROPERTIES OF POLYMER THIN FILM COATINGS, D. Patel, M. V. Fedoryshyn and Ashok Kumar Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL.

Polymers are used in variety of tribological and electronic applications due to their low coefficient of friction, high durability and low dielectric constant etc. Thin film coatings of polyimide (PI) and Polytetrafluoroethylene (PTFE) are grown on Si (100) and Corning glass (7015) substrates by pulsed laser deposition method. The films were deposited at room temperature to 450°C range. The structural and surface morphological properties have been evaluated using Fourier transform infrared spectroscopy, scanning electron microscopy and atomic force spectroscopy techniques. The mechanical properties of these coatings have been measured using nanoindentation technique. The measured mechanical properties (both hardness and Young's modulus) of these polymeric coatings have the highest values as reported so far in literature.

V10.9 IN SITU CHARACTERIZATION OF STRESS DEVELOPMENT AND RELAXATION OF GELATIN FILM DURING CONTROLLED DRYING. Mengcheng Lu\textsuperscript{1}, Si-Yue Tan\textsuperscript{2}, Randy Schunk\textsuperscript{2} and C. Jeffrey Brinker\textsuperscript{1,2}. Advanced Materials Laboratory, University of New Mexico/NSF Center for Micro-Engineering Materials, Albuquerque, NM, \textsuperscript{2}Sundin National Laboratories.

Drying of gelatin film is studied by an in-situ cantilever beam method, which observes the stress development, film shrinkage and compositional change during drying process. A gelatin film experiences stress relaxation during drying process, the relaxation could be visco-elastic relaxation or plastic deformation of polymers. In this presentation, experiments are carried out under different drying conditions, such as drying extent variation, drying rate variation. Drying stress induced plastic deformation is observed. However, the plastic deformation is accompanied by visco-elastic relaxation, which complicates the finding of the yield stress.

V10.10 ANISOTROPIC PLASTIC DEFORMATION VERSUS NEWTONIAN FLOW IN COLLOIDAL THIN FILMS DURING ION IRRADIATION. E. Stocker\textsuperscript{2}, A. van Bladeren\textsuperscript{3}, T. van Dillen\textsuperscript{4}, C. van Kuijk\textsuperscript{4}, M.L. Brogersema\textsuperscript{5} and A. Polman\textsuperscript{5}. “FOM-Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands; \textsuperscript{6}Debye Institute, University of Utrecht, THE NETHERLANDS.

Ion irradiation can be used to reduce the mechanical stress in a constrained thin film by radiation-enhanced Newtonian plastic flow, a process driven by the stress, with the atomic mobility required for the plastic transformation provided by the ion beam. Conversely, at high ion energies (> 2 MeV) the ion beam can also lead to the generation of high stress. In this case the stress originates from the amorphization of the thermal spike induced on the ion track at high electronic excitation density (> 2 keV/μm). When both the amorphous stress generation and Newtonian plastic flow act, a dynamic multilayer system is formed. The stress state is dominated by compressive stress state. Using sensitive in-situ wafer-curvature measurements during 4 MeV Xe ion irradiation of SiO\textsubscript{2} thin films we have identified the various stress components and parameters in these multi-layer systems, and unraveled their interplay.

Next, experiments were done on thin films of colloidal particles of SiO\textsubscript{2}, ZnS, TiO\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4} with diameters in the 100-200 nm range. At low colloid densities we find a dramatic microstructural deformation of the particles during irradiation, in which the diameter increases in the direction perpendicular to the ion beam, and decreases in the direction of the beam. As the particles are unconfined, no stress build up during this plastic deformation, and the shape of the colloids can be continuously tuned. By using irradiations at multiple incident angles, oblate and prolate shaped particle shapes can be made. At high colloid density, when they form a two-dimensional hexagonal crystalline structure, interaction between the particles causes the film to deform in a way that depends on the relative orientation between the crystal orientation and the ion beam. We will show that by engineering these stress-induced deformation phenomena, novel self-assembled lithographic masks and materials with interesting photonic properties can be made.

V10.11 TENSILE STRENGTH AND FRACTURE OF PASSIVE OXIDE FILMS ON METALS. M. Pung, D.E. Wilcox, and D.E. Baker, Mechanical and Materials Engineering, Washington State University, Pullman, WA.

Many metals owe their corrosion resistance to the presence of a thin passive film on the underlying metal which effectively isolates the reactive metal from the surrounding environment. These films usually between 1 and 100 nm thick, making it difficult to isolate the mechanical properties of the film from the substrate. In these cases, however, it is possible to evaluate the stress at fracture of the film using nanoindention techniques. Many of the prior studies which have examined these properties have been on single crystal metals. However, many of the corrosion resistant alloys are difficult to fabricate in single crystal form and it therefore of interest to extend these testing methods to polycrystalline materials. Passive films have been grown electrochemically on a polycrystalline titanium alloy. By varying the growth rate and applied voltages, the film thickness and structure can be controlled. Higher growth rates lead to relatively uniform film, effectively independent of the underlying oxide. Slow growth rates produce films which are crystallographically related to the underlying grain. The stress at which oxide film fracture occurs is correlated to film thickness and film structure. In situ film growth has been used to track the variations in average film properties. Observations in situ film fracture measurements on single grains during film growth show the strength of the film constant in environments in which the film is inert, but decreases by approximately an order of magnitude in solutions which lead to corrosion. The fracture mode observed was intergranular using atomic force microscopy, and is shown to qualitatively match the largest tensile stresses which develop using elastic contact mechanics.

V10.12 FRAGMENTATION BY CRACKING IN BRITTLE FILMS. Vasey Ghararie, School of Physics, MARC, University of Melbourne, Ferntree, Melbourne, AUSTRALIA

Thin films deposited on various substrates are often cracked due to a mismatch in thermo-mechanical properties of the film and substrate materials. The density of cracks can vary in a wide range depending on the mechanical properties, structure, deposition method and geometrical parameters of the film. In this study we identify major factors and properties which govern the fragmentation process in thin brittle films and evaluate the relation between the crack density, thickness and thermo-mechanical properties of the films. In the study the fragmentation process is considered by analyzing tensile stresses formed in the films during cooling from the deposition temperature and a subsequent stress relaxation following cracking. The continuum mechanics equations are used to evaluate the fragmentation size (crack density) as a function of the deposition temperature, thickness and thermal mechanical properties of the films. Theoretical data on crack density are demonstrated to be in agreement with experimental results for the carbon-nitrogen thin films of variable thickness deposited using the pulsed plasma deposition technique.

V10.13 STRESS EFFECT ON STRENGTH PROPERTIES FOR A MORPHORUS \( G_{50} A_{4} S_{4} A_{4} \) AND \( G_{50} A_{4} S_{5} A_{4} F_{7} \) THIN FILMS.
The effect of thermal stress arising from the difference in linear thermal expansion coefficient of substrate and film materials on adhesion and shear strength for thermally deposited amorphous Ge, a-Au, and Al films has been studied. Films were deposited at different deposition conditions onto heated Si, SiO₂, Zr, Te, and Hf₃N₃ substrates of optical quality. Adhesion and shear strength measurements have been carried out using a three-point bending method. Adhesion has been determined by the normal pull-off of the separated part of the film. Shear strength has been determined by the application of the external force (alongside the pin radius) normal to the film surface resulting in film shearing. Thin film deposition rate and substrate temperature effect on the adhesion and shear strength values have been investigated. It has been found that the adhesion and shear strengths were different for thin films deposited onto different substrates in similar deposition conditions, the adhesion and shear strength being in direct proportionality. To account for the obtained results the data on the electron microscopy structural investigations and film stress measurements have been used. It has been shown that the found correlation between adhesion and shear strength resulted from the constituent of thermal stresses directed across the interface and separation of the film from the substrate took place along the transition layer and thus was of cohesive nature.

**V10.14**

**STRESS CORROSION CRACKING OF STAINLESS STEEL: THIN FILMS**

Robert E. Zien, Thomas M. Devine, University of California, Dept. of Materials Science and Mineral Engineering, Berkeley, CA.

Structural materials employed in applications that require long service life in environments, especially in the presence of corrosion and cracking, must be resistant to the initiation of stress corrosion cracking. In particular, because of the ubiquitous nature of chloride ions, the corrosion must be resistant to initiation of SCC in chloride-ion media. In this study, the initiation of stress corrosion cracking of 304 stainless steel in 0.75M HCl was investigated by thin film samples that were chemically selected to mirror the environment and atmosphere. The tests were carried out using a pin on disc method. The samples were exposed to 0.75M HCl and stressed in tension by two different methods. In the first method, the stress corrosion cracking test was carried out by using a square shaped hole measuring 3 mm x 3 mm. The substrate was then separated into the silicon substrate, creating an unsupported thin film sample of stainless steel. The thin film samples were exposed to 0.75M HCl and stressed in tension by two different methods. In the first method, the stress corrosion cracking test was carried out by using a square shaped hole measuring 3 mm x 3 mm. The substrate was then separated into the silicon substrate, creating an unsupported thin film sample of stainless steel. The thin film samples were then exposed to 0.75M HCl and stressed in tension to observe the initiation of stress corrosion cracking.

**V10.15**

**THREE-DIMENSIONAL MODELING OF FILM-EDGE-INDUCED STRESS IN SILICON DEVICE STRUCTURES FOR THE ANALYSIS OF LAYOUT-DEPENDENT DISLOCTION GENERATION**

Igor V. Vedeneev, The University of the West Indies, Mona, Jamaica; Konstantin V. Lekoe, Dallas Semiconductor, Dallas, TX; Thomas Schaefer, Fraunhofer USA Resource Center, Ann Arbor, MI.

Many processes of microelectronic device fabrication initiate high mechanical stress in the device structures. Localized stresses at film edges are particularly large and, consequently, semiconductor substrates with patterned and embedded films often suffer from dislocation generation. The crystalline quality of device elements manufactured using 0.35 and 0.25 um CMOS process technologies with LOCOS and STI isolation has been studied. Localized dislocation generation has been regularly detected in layout-specific regions at film edges. To find the cause of the observed premature growth of dislocation generation, stresses induced by patterned and embedded films in the device structures with complex layouts were analyzed. A three-dimensional model of stresses was developed for this purpose. Numerical approximations were applied with modifications aiming to avoid a singularity problem and improve accuracy. Notwithstanding the simplifying assumptions, the performed analysis of stresses in device structures was consistent with the experimental observations of layout-dependent dislocation generation. The stress-intensive factor of stress distribution, i.e., the extent of regions subjected to high resolved shear stresses, is found to correspond to critical layout features, which are responsible for the vulnerability of device structures to dislocations.

**V10.16**

**STRESS EFFECTS ON AI AND Al-Cu THIN FILM GRAIN BOUNDARY DIFFUSION**

X.-Y. Liu and C.-L. Liu, Motorola, Inc., Los Alamos, NM.

Stress effects on grain boundary diffusions in Al and Al-Cu thin films have been calculated atomically. Energetics as a function of stress were calculated for various stress magnitudes and interstitial migration. The bulk values calculated are in excellent agreement with experimental data. We will discuss the calculation methods and also discuss the strain state effect. Finally, the impact of electromigration is pointed out based on the grain boundary results.

**V10.17**

**MECHANICAL FRICTION FORCE MEASUREMENT OF THIN FILMS PREPARED BY CO-SPUTTERING DEPOSITION TECHNOLOGY**


Low friction coefficients under very low load is required for the surfaces of thin films for near contact storage media system and micro machine system. Friction strongly depends on the surface conditions and structures of thin films. It is therefore important to measure friction coefficient accurately in-situ in the atmosphere controlling parameters of such surface conditions as contaminants layer, adsorbed layer and oxider layer by changing load and pressure. We have developed a mechanical friction measurement technique to evaluate sliding friction coefficient under changing load from 1 N down to less than 1 mN and atmospheric pressure from about 100 kPa down to 10 kPa. The measurement was carried out on such materials as stainless steel, copper, and copper film on stainless steel, nitride sintered plate and titanium nitride coated steel. Boron nitride segregated copper film on steel was prepared by co-sputtering deposition technology. Boron nitride and copper targets were sputtered at the same time and the boron nitride supersegregated into copper film can uniformly segregate boron nitride with hexagonal crystal structure on the surface of the film. Compressed stress induced inside the film can make the crystal plane of boron nitride parallel to the film surface. The friction measurement shows the friction coefficient of boron nitride surface segregated copper film keeps smaller in decreasing the pressure and in decreasing the load than any friction coefficients among them.

**V10.18**

**MECHANICAL PROPERTIES AND ADHESION OF PZT THIN FILMS FOR MEMS**

J. M. Jung, Mechanical and Materials Engineering, Washington State University, Pullman, WA; B.T. Crozier, Mechanical and Materials Engineering, Washington State University; A. Bandyopadhyay, Mechanical and Materials Engineering, Washington State University, Pullman, WA; N.R. Moody, Sandia National Laboratories, Livermore, CA; and J. J. Kulikowski, Mechanical and Materials Engineering, Washington State University, Pullman, WA.

Piezoelectric films are attractive materials for use in microelectromechanical systems (MEMS) due to their ability to act as both sensors and actuators. One of the primary modes of deformation is the deflection of lead zirconate titanate (PZT) beams and membranes, where the adhesion of the film is critical for the reliability of the device. Thin films of PZT between 250 and 750 nm have been grown via solution deposition routes onto platinum silicon. The films have been tested using microindentation and scratch testing techniques. Three failure mechanisms in these films have been observed. Indentation induced delamination at the PZT - Pt interface occurs after the indentation tip is removed from the film when loads between 1 and 10 mN are applied to the sample; delamination while the indentation tip is in contact with the film occurs at approximately 10 mN; and scratching induced delamination in front of the indenter tip at normal loads above 4 mN. At large loads, failure can be generated by the underlying sputtered oxide film and the silicon substrate. Each of these failure modes has a different mechanism solution, the results of all three mechanisms are compared to determine the both the residual stress and adhesion energy of the films. These results are compared to x-ray diffraction measurements of strain in the films. Fracture around the delaminated regions has been examined using scanning probe and electron microscopy. Free standing PZT membranes above micro machined cavities have been mechanically deformed to examine the mechanical response and failure modes in these structures. The adhesion of the films improves with increased crystallization time. Auger electron microscopy has shown that films crystallized for longer periods of time do not have significant diffusion across the PZT - Pt interface. Processing, mechanical properties, and failure modes in these devices will be discussed.

Multilayer metallic thin films are used for a wide range of applications in the microelectronics industry. Examples span from the multilayer metal stack used in or more recently CVD interconnects at the chip-level to underbump metallization in flip chip packaging technology. Multilayer metal/oxide films are now commonly found in various stages of surface micro-machining, based MEMS technology. In such applications, the oxide layer plays the role of a sacrificial layer that is removed during subsequent processing, which ultimately results in the fabrication of movable structures. Alternatively, metallic films can also be used as sacrificial layers. During the processing of such multilayer structures, thermal excursions of previously deposited layers is inevitable and hence affects the microstructure and properties of such layers. Phenomena such as grain growth, interdiffusion, intermediate phase formation, and recovery processes can become active due to the thermal excursion that occurs during the various deposition and etch processes used in microfabrication. In the current study, we have examined the microstructural changes associated with the deposition of a multilayer metal stack sandwiched between oxide layers on a Si substrate, a combination used in the fabrication of an actuator. The multilayer metal stack consists of Au and Al (Cu) layers separated by a Ti barrier layer. This will address the role of interdiffusion and stress relaxation that occur during processing in influencing the integrity of the layers. The effect of the thickness of the barrier layer will also be outlined in the present implication of such microstructural changes for MEMS device processing, in particular, the actuator, will be highlighted.

VI.20 EFFECTS OF SEEDING OVER THE MICROSTRUCTURE AND STRESSES OF DIAMOND THIN FILMS. S. Gupta, G. Morel, R. S. Kastner, Univ. of Puerto Rico, Dept. of Physics, San Juan, PUERTO RICO; D.R. Gilbert, R.K. Singh, Dept. of Materials Science and Engineering, Univ. of Florida, Gainesville, FL.

We have studied diamond films grown at low pressure (1.0 Torr) and temperatures (550-700°C) by electron cyclotron resonance (ECR) assisted chemical vapor deposition (CVD). These films were grown on seeded Si(100) substrates with different seeding densities: 0.001, 0.01, 0.1, 1.0, and 10%. Raman spectroscopy (RS), scanning electron microscopy (SEM), spectroscopic ellipsometry (SE), and X-ray diffraction (XRD) were employed to investigate the crystalline quality, diamond yield, void fraction, and stresses developed in these films. The thermal interfacial stress, interactions across grain boundaries, and internal stress were considered in order to account for the total stress in the film. The layer-by-layer and microvoid fraction of these films were characterized by SE. We present correlations among seeding density, relative amount of non-diamond phase, O/C ratio, grain size, internal stress, and total stress. These results outline the best surfacing condition for diamond film deposition. Authors wish to gratefully acknowledge the following NSF-DMR-8817595 US Grant for financial assistance.

VI.21 TRANSFERRED TO V7.7/UL10.7

VI.22 MICROMECHANICAL ANALYSIS OF RESIDUAL STRESS EFFECT IN CVD-PROCESSED DIAMOND WAFERS. Jeung-hyun Joeng, Dongil Kwon, School of Materials Science and Engineering, Seoul National University, Seoul, SOUTH KOREA; Jong-Kap Lee, Young-Hee Lee, National Technology Research Center, Korea Institute of Science and Technology, Seoul, SOUTH KOREA.

Diamond wafer has been considered as promising material for electronic substrate, thermal spreader, etc. because of its high thermal conductivity and low electrical conductivity as well as high strength. It has been made using CVD process such as microwave plasma (MPCVD), DC plasma (DCCVD) and hot filament assisted (HFCVD). However, high residual stress of diamond film induces bowing and through-thickness cracking in thick diamond wafer, and hampers the economic fabrication of the wafer. Thus, to investigate the causes of bowing and cracking the measurement of residual stress is studied first of all. Of the residual stress, in particular, intrinsic stress is one of the most issued research topics because its effect on wafer-related problems is dominant though the magnitude is relatively small. Quantitative stress analysis is required. One is that it is very small compared to thermal stress when diamond is deposited onto metal substrates such as Mo, Ti, and W. Thus, Si substrate with similar thermal expansion coefficient to diamond is often used for the measurement of intrinsic stress. However, another problem is that high-temperature plastic deformation of Si substrate reduces the initial stress during deposition but enlarges the curvature, which makes it difficult accurate estimation of residual stress. The latter problem is solved through beam bending model and numerical calculation in which plastic deformation of Si is involved. In the method, intrinsic stress of film and yield stress of Si can be evaluated from the apparent curvature of substrate measured just after deposition before diamond film. This is verified by Raman and XRD method. The analysis is carried out on several specimens of different thickness deposited at 1223K under the atmosphere of CH₄ and H₂ gas at PCVD by MPCVD. Bowing and curvature measurement results and literature data, causes and effects of thickness dependence of intrinsic stress are discussed.

VI.23 RESIDUAL STRESSES IN MEMS STRUCTURES. Bhaskar S. Majumdar, UES, Inc./AFRL, Materials Directorate, William J. Covarr, Nicholas J. Pagano, Materials Directorate, AFRL, Wright Patterson Air Force Base, OH.

Residual stresses impose major restrictions on the performance of MEMS devices. We have focused our attention on square and circular micro-mirrors that are supported by electrically activated arms. Permanent curvature in such mirrors seriously impair mirror performance. In this work, the residual stresses were estimated from curvature measurements on different sized beams using an interferometric technique, complemented by rigorous elastic analysis of complete beams. It is notable that typical residual stress analyses is based on Stoney’s equation for a thick substrate, which is not valid for the thin MEMS structures. Mirror structures consisted of polycrystalline silicon (polycrystalline), poly1, poly2, poly1+poly2, poly2+Au, and poly1+poly2+5 nm thick TiN on the thickness between 0.5 - 3 microns, where the poly refers to polycrystalline with different amount of dopant. Beam sizes ranged from slender beams with large length-to-width ratio, to square mirrors. Analysis of the beams allowed a consistent estimate of the stress-free temperature for the films associated with the Au coating. Also, results from the slender beams agreed with those from square mirrors. In addition to the thermally induced residual stress, there is a thermal component of the residual stress which generally depends on the processing conditions. Under epitaxial conditions, they often give rise to interfacial dislocations that are difficult to annul out. In order to decouple the thermal and process component of the residual stresses, curvature measurements were conducted at different temperatures. With increasing temperature, the beams associated with the gold coating straightened out, and in some cases they took an opposite curvature. Correspondingly, the poly1+poly2 beams, whose curvatures were primarily process related, showed negligible change in the beam curvature. The results and analysis technique will be presented in detail, including a video presentation of the changing shape of the beam, and possible methods to reduce the residual stresses will be discussed.

VI.24 STRESS AND STRESS RELAXATION STUDY OF SPUNNED PZT THIN FILMS FOR MICROSYSTEMS APPLICATIONS. Emmanuel DeFi, Christophe Malhure, Christiane Dahois, Daniel Bixier, Laboratoire de Physique de la Matière, INSa de Lyon, FRANCE.

Thin PZT films on silicon substrates are of great interest for the realization of micro-machined actuators used in micro-electromechanical devices like micro-pumps. The stresses induced by a deposition process have to be determined in order to know their influence and even affect the performances and reliability of membrane-based systems. In this paper we present a study of the stress and its relaxation for the PZT films, and associated electrodes, deposited on oxidized silicon substrates. The stress in the films is calculated from the bending plate method and the Stoney’s equation. The radius of curvature were measured by optical profilometry before and after films deposition. The substrates (180µm Si + 0.66 µm thermal SiO₂) were coated with sputtered Ti (20 nm) and Pt (200 nm) used as bottom electrode. The global stress in the Ti/Pt layer was found compressive (-1.5 GPa) after deposition and tensile (500 MPa) after annealing (480°C, 3h, Ar). A 1 µm thick PZT layer was RMS magnetron sputtered and crystallized by HFIA (700°C, 3h, Air). The deposited PZT films exhibited a little tensile stress of 10 MPa. After annealing, a tensile stress value of 400 MPa was found. Moreover, the stress values were found to be dependent of the annealing temperature to the deposited films of the PZT layer obtained, as determined by X-ray diffraction. Finally, we observed that the stress of the whole multilayer showed an exponential decrease as a function of time. In order to explain this phenomenon, depth profile of each component of the PZT layer was obtained by Secondary Ion Mass Spectrometry (SIMS). This
time-dependent stress relaxation was then correlated to a load and oxygen migration across the PZT layer.

SESSION VI: NANOINDENTATION AND ANGULAR PULSED TESTING WITH NON-LEAKY INTERFACE

Chair: Barry N. Lucas and Tim P. Weihs
Friday, December 3, 1999
Room 306 (H)

8:30 AM #VIII.1
A SIMPLE MODEL FOR PILE-UP DURING INDENTATION BY A RIGID CONE. Hai Tao Song, Rice University, Dept. of Materials Science, Houston, TX; George M. Pharr, The University of Tennessee, Dept. of Materials Science & Eng. and Oak Ridge National Laboratory, Metals & Ceramics Division, Knoxville, TN.

Recent experimental and analytical studies have shown that the indentation pile-up, which occurs primarily in soft metals with little or no tendency to work harden, can significantly affect the accuracy with which their mechanical properties can be measured by load and depth sensing indentation methods (nanoindentation). Pile-up affects the contact depth and the contact area in a manner which is not accounted for in current indentation data analysis procedures. A simple model is presented which can be used to predict the amount of pile-up in elastoplastic materials indented by a rigid cone. The model essentially provides means for interpolating between two limiting behaviors with well-known solutions: purely elastic and rigid-plastic contact. The model compares favorably with finite element simulations and can also be used to directly relate the indentation load to the yield stress and elastic modulus. The utility and limitations of the model are discussed.

Research sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

9:00 AM #VIII.2
A STUDY OF THIN FILM INDENTATION BY MECHANISM-BASED STRAIN GRADIENT PLASTICITY. Y. Huang, Z. Xue, Univ of Illinois, Dept. of Mechanical Engr; Urbana, IL; H. Gao, Stanford Univ, Div of Mechanics and Computation, Stanford, CA.

Plastic deformation exhibits strong size dependence in micron and submicron structures. Two hardening mechanisms have been proposed to account for such size dependence. The first mechanism, called strain gradient plasticity, is based on the assertion that gradients in the plastic strain field induce extra stored defects called geometrically necessary dislocations. These extra defects trap the motion of statistically stored dislocations and increase the work hardening. The second mechanism, called structural confinement effect, assumes that dislocation motion in a confined small volume is more difficult. We have recently proposed a theory of mechanism-based strain gradient (MSG) plasticity to account for the first mechanism. This theory builds upon Taylor hardening model incorporating geometrically necessary dislocation idea. Here we apply the MSG theory to study a thin film deforming plastically under micro-indentation. We compare the experimentally measured indentation hardness with the theoretical predictions based on MSG theory and classical plasticity. We will also discuss the effects due to structural confinement.

9:15 AM #VIII.3
NANOINDENTATION EXPERIMENTS ON MONOCRYSTALLINE AND POLYCRYSTALLINE METAL FILMS ON SUBSTRATES: EFFECTS OF FILM THICKNESS AND CRYSTALLOGRAPHIC ORIENTATION. A. Goulstone, A.E. Giannakopoulos, S. Suresh and K-Y. Zeng, MIT, Dept. of MS and E, Cambridge, MA.

We present results from systematic nanoindentation experiments performed on polycrystalline Al and Cu thin films of known texture and thickness deposited on Si substrates. In addition, experimental results from nanoindentation of single crystal Al thin films of different orientations are also presented. Particular attention is devoted to the extraction of nanoindentation response in the thin films which is not affected by the indenter tip radius. Both single-crystal and polycrystalline metal films, 500 to 1000 nm in thickness, and of different known crystallographic orientations, exhibit multiple, sudden bursts of indenter penetration displacements [h] at a constant indentation load [P] under nanoindentation. It is reasoned that these displacement bursts are induced by the emission of dislocations in the thin films. The load for the onset of the first dislocation burst, which is independent of film thickness, is shown to occur when the computed maximum shear stress at the indenter tip approximately equals the theoretical shear strength of the metal films for all the tested cases examined. It is demonstrated that the overall plastic response of the thin film subjected to nanoindentation is composed of purely elastic response with intermittent microplasticity during which the indenter "sinks in" to the film while the metal "piles up" around the indentation perimeter.

9:30 AM #VIII.4
FINITE ELEMENT AND ANALYTICAL MODELING OF NANOINDENTATION: RESULTS OF W FILMS ON SAPPHIRE AND Al SUBSTRATES. Rangdoga Y. Saha and William J. Wooldridge, Dept. of Materials Science and Engineering, Stanford University, Stanford, CA.

Determination of the mechanical properties of thin films on substrates by indentation has always been a problem because of the influence of the substrate on measured properties. In this paper we revisit this problem and examine various approaches that have been developed in recent years. W films with thickness ranging from 0.5 micrometers to 2.1 micrometers were deposited onto sapphire and Al substrates. Hardness and modulus of the two film/substrate systems were determined by nanoindentation. As expected, the hardness values were observed to match up at small indentation depths (< 10% of film thickness). But as the depth of indentation increased, the values deviated towards the respective substrate values. Elastic modulus, on the other hand, matched up only at extremely shallow displacements (< 30nm). Finite element analyses (FEA) was used to analyze the indentation behavior of these film/substrate systems. The yield strength of the film was varied until a good fit between the FEM analysis and experimental load-displacement data was found. The resulting hardneses were then compared with experimental and finite element values. Excellent agreement was observed. These differences can be explained by the inability of the Oliver-Pharr analysis of the experimental data to account for pile-up and pile-in effects.

Analytical modeling of the elastic modulus was also attempted by using an equation suggested by Hunsinger and Nix. We also examined the correctness of the Sneddon solution proposed by Hay and Pharr.

9:45 AM #VIII.5
DETERMINING ELASTIC MODULUS AND HARDNESS FROM THE WORK OF INDENTATION USING CONICAL AND PYRAMIDAL INDENTERS. Yang R. Cheng, General Motors R&D Center, Warren, MI; Chien-Min Cheng, Institute of Mechanics, Beijing, China.

A method for obtaining the elastic modulus and hardness of materials using instrumented indentation with conical and pyramidal indenters is proposed. This method is based on a recently established relationship between elastic modulus, hardness, and the work of indentation for elastic-plastic solids with work-hardening [1]. It was shown that the ratio of hardness to elastic modulus scales with the ratio of irreversible work to total work of indentation. The ratio of hardness to elastic modulus can then be obtained directly from measuring the work of indentation. Together with a well-known relationship between elastic modulus, initial unloading slope, and contact area, a new method is then suggested for estimating the hardness and modulus of solids using instrumented indentation with conical or pyramidal indenters [1]. Y-T. Cheng and C-M. Cheng, Appl. Phys. Lett. 73, 614 (1998).

10:00 AM #VIII.6
QUANTITATIVE STUDY OF NANOSCALE CONTACT AND PRE-CONTACT MECHANICS USING FORCE MODULATION. S.A. Syed Asif, Materials Science and Engineering, University of Florida, Gainesville, FL; K.J. Vahso, R.J. Colton, Chemistry Division, Naval Research Laboratory, Washington, DC.

For sub-micron scale mechanical property measurement, depth sensing nanoindentation techniques are very successful and gaining much attention. However, for ultrasmall volumes of materials below a length scale of 10nm measuring the quantitative mechanical properties of material is still a problem. The atomic force microscope (AFM) has very good surface sensitivity and has been shown to measure nanomechanical properties. However cantilever instability, conventional force detection and depth-sensing techniques (inferred from the known spring constant of the lever), make contact area measurements difficult, hence the measured mechanical properties are usually only qualitative. In this presentation we show that combining force modulation with depth-sensing nanoindentation allows measurement of the mechanical properties of materials on the sub-nanometer scale. The stiffness sensitivity of the technique is ~1.0 N/m, which is sufficient to detect nanoscale surface forces and locate the surface of compliant materials. With this method we have measured the mechanical response of silicon surface in four different regimes, the pre-contact, apparent contact, elastic contact and the elastically deformed contact. We also report a novel technique for stiffness imaging technique, which can be used directly to map the mechanical properties of materials with sub-micron lateral resolution.
10:45 AM V11.7
MICROBRIDGE TESTING OF SILICON NITRIDE THIN FILMS.
Tung-Yi Zhang, Long-Qing Chen, Yuan-Jing Su and Chi-Fu Qian
Department of Mechanical Engineering, Hong Kong University of
Science and Technology, Clear Water Bay, Kowloon, Hong Kong,
CHINA.

The present work proposes a novel microbridge testing of thin films. Samples for the microbridge testing are prepared with the microelectromechanical fabrication technique such that they are easy to handle. The microbridge testing is conducted with a load and displacement sensing nanodiscrete system equipped with a microscope. The problem of large deflection of the microbridge is solved analytically and numerically. The relationship of load-deflection is also a function of the residual stress, the Young's modulus and the sample geometry. Fitting an experimental entire load-deflection curve with the theoretical one results in the Young's modulus and residual stress of a thin film. Furthermore, the bending strength of the film is determined from the critical load at fracture by the proposed method. Silicon nitride films fabricated by low pressure vapor deposition are serve as a model system to verify the proposed method. The experimental results show that the theoretical load-deflection relationship perfectly fits the entire experimental load-deflection curves and characterizes the Young's modulus, residual stress and bending strength.

Supported by the Hong Kong Research Grants Council.

11:00 AM V11.8
MECHANICAL SPECTROSCOPY OF COPPER THIN FILMS
DEPOSITED ON SILICON SUBSTRATES. J. Kehl, M. Weller, E.
Arzt, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY.

The elastic and plastic properties of unpassivated copper thin films were studied by mechanical spectroscopy. Specimens with dimensions of 50x0.5 mm were prepared from oxidized silicon wafers with additional 50 nm silicon nitride layers acting as diffusion barriers. Thin copper films with 1, 2 and 4 μm thickness were prepared by magnetron sputtering. A new resonant bar apparatus was developed in which the specimens are excited to flexural eigenfrequencies. For electrostatic drive and detection a thin 50 nm platinum film was sputtered on the opposite side to the copper film. Internal friction (Q^{-1}) and resonant frequency (f) of the composite were measured as a function of temperature with heating and cooling cycles between 150 K and 800 K. The damping of the silicon substrate was measured separately, thus allowing to determine the damping of the film alone. The damping spectra of the composite specimens exhibit a relaxation maximum around 600 K which increases with the film thickness. The underlying relaxation mechanism is discussed with respect to grain-boundary and self-diffusion. Measurements of the resonant-frequency give information on the temperature variation of Young's modulus and the adhesion between film and substrate. The aim of the present studies is a better understanding of the damage mechanisms (electromigration, fracture) in thin film systems.

11:15 AM V11.9
STRESS MEASUREMENTS IN THIN METAL FILMS WITH
PICOSECOND ULTRASONICS. G. Andrew Antonelli, Intel Corp.,
Portland, OR and Brown Univ., Dept. of Physics, Providence, RI;
Humphrey J. Marc, Brown Univ., Dept. of Physics, Providence, RI.

We have developed an apparatus which can be used to make very accurate measurements of the transit time of an ultrashort sound pulse through a thin metal film. When the temperature of the film is changed, there is a change in transit time arising from the variation of the sound velocity with temperature. In addition, the sound velocity and transit time are modified by thermal stress in the film that results from the difference in the thermal expansion coefficients of the film and the substrate. As a result, accurate measurements of the transit time as a function of temperature make possible the study of the thermal stress in the metal film and the relaxation of this stress. We will report results for a number of different film/substrate combinations.

This work has been supported by the Intel Corporation and the Department of Energy.

11:30 AM V11.10
MEASUREMENT OF LOCAL STRAIN IN THIN ALUMINUM INTERCONNECTS USING CONVERGENT BEAM ELECTRON DIFFRACTION (CBED). Stephan Kramer and Joachim Meyer, Max-Planck-Institut f. Metallforschung, Stuttgart, GERMANY.

The local variation of lattice strain in multicomponent systems plays an important role in damage formation. Interesting aspects are for example the grain-boundary strain or the strain development during electromigration. Convergent beam electron diffraction (CBED) makes it possible to measure the lattice parameter with high spatial resolution (16 Å) in interconnects with widths smaller than 400 nm. Accuracies down to 10^{-4} can be achieved. In the present investigation we have measured thermal strains in Al interconnects. The experiments were performed on a Zeiss EM 912 Omega EFTEM using a liquid nitrogen double tilt cold stage and the diffraction patterns were recorded with a slow scan CCD camera. TEM specimens were prepared using standard techniques or with the help of a focused ion beam (FIB) scanning microscope. Measuring the HOLZ (higher order Laue zone) line positions in CBED patterns makes it possible to analyse the three dimensional strain state in interconnects. High accuracies can be achieved when the line positions are measured at sub-pixel accuracy and the dynamical interaction of the electrons with the sample are taken into account properly. We have performed temperature dependent measurements of the strain state of unpassivated interconnects in a temperature range between -170° C and +100° C. Comparison with finite element models shows that the strain state can be well explained using elastic models and measured thermal expansion coefficients. In addition, it is seen that the accuracy of the measurement is sufficient to obtain quantitative information about the surrounding material and constraints on the interconnect. Future experiments include in-situ measurements of the strain evolution during electromigration testing.

11:45 AM V11.11
APPLICATION OF COMBINED WHITE/MONOCHROMATIC
X-RAY MICROBEAM TECHNIQUES FOR THE STUDY OF
TEXTURE AND TRIAXIAL STRAIN/STRESS IN MATERIALS.

The availability of high brilliance 3rd generation synchrotron sources and recent advances in low focussing mirror technology have made possible a new x-ray microbeam technique combining white and monochromatic capabilities for the study of texture and triaxial strain/stress in materials at micron or sub-micron levels (mesoscale). As samples are scanned beneath the microbeam, reflections are collected using a CCD camera detector, which avoids the surface of confusion problem of conventional diffractometer techniques. The high potential of this non-destructive technique comes from the fact that the orientation and the full deviatoric strain tensor of the illuminated area can be derived from a single Laue pattern. It is particularly suitable for grain-to-grain and intragranular analysis of materials at the submicron level. The penetrating power of hard x-rays also gives rise to the possibility of orientation and strain profile investigations as a function of depth. Methods used in implementing these techniques on the MHATT-CAT beam line at the Advanced Photon Source will be discussed and applications of this technique will be presented. (Interconnects, deformed samples, thin films). *Research sponsored by the U.S. Department of Energy under contract DE-AC05-86OR22464 with Lockheed Martin Energy Research Corp. N. Tamura and J.-S. Chung are supported under the ORNL Postdoctoral Research Associates Program administrated jointly by ORNL and OHSE. The x-ray measurements were performed on the MHATT-CAT beam line at the APS. The APS is supported by the DOE Office of Energy Research under contract W-31-109-ENG-38.

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