SYMPOSIUM V

Thin Films–Stresses and Mechanical Properties VIII

November 29 – December 3, 1999

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* 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. Frans Spaepen, Division of Engineering and Applied Sciences, Harvard University, Cambridge MA.

Recent progress in the measurement of interface stresses is reviewed. There are now three independent determinations of 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 show that roughness may account for the lower interface stress measured in multilayers with the smallest repeat lengths. The effect of the interface 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 Shandards and Technology, Gaithersburgh, MD; Ingrid X. Shao and Robert C. Cammarata, 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 quantity that determines the magnitude of this stress is the interface stress. It equals the derivative of the free 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 (0001) titanium layers using transmission x-ray diffraction studies of freestanding aluminum/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. A. Misra, M. Verdier, H. Kung, J.D. Embury and J.P. Hirth, Los Alamos National Lab, Materials Science and Technology Division, Los Alamos, NM.

Metallic multilayers provide the opportunity to synthesize materials close to the theoretical strength and investigate 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 (Hall-Petch), discrete pile-up (modified Hall-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 grain size ranges over which different deformation mechanisms operate. These maps are intended to be guidelines for interpreting the scale-dependent strengthening or softening mechanisms in mutlilayers. 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 ANALYSIS OF RESIDUAL STRESSES AND BENDING STRESSES IN FREE-STANDING Nb/Nb_5Si_3 MICROLAMINATES. 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 microlaminates are currently being developed to serve as thin ($\sim$300μm) outer walls in future, high-temperature turbine blades. Controlling and limiting the thermal stresses and bending stresses in these composites will be critical to their performance. Here we present an X-ray analyses of these stresses in a model microlaminate system that contains many micron thick layers of Nb and Nb_5Si_3. The samples were sputter deposited at room temperature, removed from their substrates, and then annealed at 1200 °C for 3 hours. The residual stresses and bending stresses in the individual layers were then quantified after cooling using nonsymmetric X-ray diffraction. Large residual stresses ($\sim$300MPa) were found in samples that were flat after annealing and these stresses are attributed to a mismatch in the thermal expansion coefficients for the Nb and Nb_5Si_3 phases. The Nb layers were in tension and the silicide layers were in compression. However, even larger (>500MPa) bending stresses were also detected in microlaminates that were curved after annealing and then were flattened for the X-ray measurements. In these samples both the upper Nb and Nb_5Si_3 layers were in compression due to the bending stresses that resulted from the flattening. By characterizing strains in the top Nb_5Si_3 layer, both normal and parallel to the bending axis, a Poisson's ratio of ν=0.194 was determined for the polycrystalline Nb_5Si_3 phase.

2:45 PM V1.5
ASPECTS OF PLASTICITY IN METALLIC MULTILAYERS. Marc Verdier, Amit Misra, John David Embury, Harriet Kung, 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 mechanical behaviour, one needs to consider factors such as difference in shear modulii, internal stress and detailed nature of interface. Thus a variety of systems can be used to control those factors such as Cu/Ni, Cu/Cr, Cu/Ag and Cu/Nb. In order to deduce the mechanical properties, dedicated experiments were designed: injection of dislocations from a single crystal substrate into the multilayer, penetration by a nanoindenter, tensile tests on free standing films, and measurements of the residual stresses. 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 ANTIFERROMAGNETIC PHASE TRANSFORMATION. B.J. Daniels, S.P. Bozeman, and H. Ha, Seagate Recording Heads, Minneapolis, MN.

The stresses in several varieties of sputter-deposited, NiMn-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 of the properties of the amorphous oxide underlayer. These films were then subjected to an anneal in an applied magnetic field for 2 hours at 300 deg C. This anneal causes the antiferromagnetic layer, NiMn, to undergo a phase transformation from the face-centered cubic (fcc) to the face-centered tetragonal (fct) crystal structure. This phase transformation increases the average stresses 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 stress 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 process. Analogous data for PtMn-based spin valve multilayers will also be discussed.

3:45 PM V1.7
THE MICROSTRUCTURE AND NANOINDENTATION BEHAVIOUR OF TiN/NbN MULTILAYERS. J.M. Molina Aldareguia, S.J. Lloyd, Z.H. Barber, M.G. Blamire and W.J. Clegg; Cambridge University, Dept of Materials Science and Metallurgy, Cambridge, UNITED KINGDOM.

TiN/NbN multilayers, with bilayer thickness between 10 nm and 50 nm and a total film thickness of 1-3 μm, have been grown by UHV reactive magnetron sputter deposition onto MgO (001), (011) and (111) substrates held at temperatures ranging from 660 °C to 800 °C. The hardness has been measured by nanoindentation and the as-deposited and deformed structures have been observed in cross-section by transmission electron microscopy (TEM). To prepare TEM specimens around the nanoindentations, a focused ion beam workstation (FIB) has been used. TEM observations of the as-deposited films showed that whilst epitaxial growth of the multilayers occurred in the first few layers, this soon breaks down giving rise to the formation of a columnar structure, with layers 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) and TEM 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 PM V1.8
INFLUENCE OF NANOMETER-SCALE MULTILAYERED THIN FILM COATING ON FATIGUE CRACK INITIATION. M.R. Stoudt and R.E. Ricker, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD; R.C. Cammarata, Johns Hopkins University, Department of Materials Science and Engineering, Baltimore, MD.

Multilayered Cu-Ni thin films were electrodeposited onto annealed polycrystalline copper cylindrical substrates. The bilayer repeat length of the multilayered coatings was 2nm, and the overall thickness of the coatings was 5 μm. 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 5 μm 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 nucleation and multiplication leading to enhanced fatigue lifetimes will be presented.

4:15 PM V1.9
PROCESSING, MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF Ni / Ni_3Al MULTILAYERED THIN FILMS. Rajarshi Banerjee, Jason Fain, Peter M. Anderson, Hamish L. Fraser, The Ohio State University, Dept. of Materials Science and Engineering, Columbus, OH.

The Ni-Ni_3Al system is the basis of a large number of Ni-based superalloys used extensively in the aerospace industry. The mechanical properties of bulk superalloys, which primarily consist of a Ni-based fcc matrix reinforced with cuboidal precipitates of Ni_3Al, have been extensively researched. The goal of the present study is to investigate the mechanical properties of multilayered Ni / Ni_3Al nanocomposites in the thin film form. These multilayers have been processed using UHV magnetron sputtering by alternate deposition of pure elemental Ni and Ni-25at%Al layers in the range of 20 nm - 120 nm. By varying the substrate material and processing parameters such as deposition temperature, multilayers with two types of interfacial orientations, (111) Ni // (111) Ni_3Al and (002) Ni // (002) Ni_3Al, have been fabricated. Microstructural and phase characterization of the 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 coherency 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 stresses. 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 / Ni_3Al multilayers, studied using nanoindentation techniques, will be discussed and compared with the fracture studies

4:30 PM V1.10
NANOINDENTATION STUDY OF AMORPHOUS METAL MULTILAYERED THIN FILMS. J.B. Vella, A.B. Mann, T.P. Weihs 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.Kung, Los Alamos National Laboratory, Los Alamos, NM.

The hardness and elastic behavior of amorphous metal multilayered thin films were investigated by nanoindentation. The systems studied were FeTi-CuNb, FeB-CuNb, and FeTi-FeB. The multiayered films were produced by sputtering onto sapphire $< 0001 >$ sbstrates. The range of bilayer repeat lengths studied was 2 nm to 50 nm, and the overall thickness of each film was about 1 μm. 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 10 nm. The implications of these results regarding the deformation behavior of amorphous metals will be discussed.

4:45 PM V1.11
THERMAL SHOCK RESISTANCE OF THIN MULTI-LAYERED CERAMIC SYSTEMS. Esteban P. Busso, Yuri V. Tkach, and Rowland P. Travis.

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 behaviour of thin multi-layer ceramic systems (approx. 10 to 200 um thick layers). An experimental procedure based on controlled specimen air 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 probabilistic-based approach to predict the thermal shock behaviour of the brittle multi-layer systems is proposed. It relies on (i) Weibull distributions of the system stresses 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. Failure diagrams are constructed from a combination of the 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
Chairs: Peter M. Anderson and Oliver Kraft
Tuesday Morning, November 30, 1999
Room 306 (H)

8:30 AM *V2.1
PLASTIC DEFORMATION IN THIN METAL FILMS. Shefford P. Baker, Cornell University, Department of Materials Science and Engineering, Bard Hall, 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 thought to arise both from the microstructure, which may be in a highly non-equilibrium 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 stress-strain characteristics induced by a particular thermomechanical treatment persisting even after subsequent treatments to higher temperatures or strain levels). These effects are seen to be very sensitive to low levels of impurities and to the presence and nature of adjacent substrate and capping layers. Elastic anisotropy is also expected to play an important role. To understand these behaviors, constraints on diffusional relaxation and dislocation motion have been invoked. In this paper, an overview of recent 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
WAFER CURVATURE STUDIES OF STRENGTHENING MECHANISMS IN THIN GOLD FILMS ON SUBSTRATES. Omar S. 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 stresses in these films are related inversely to the film thickness when the thickness is greater than about 1 micrometer. This relationship is expected from a dislocation constraint model of plasticity. However, thinner films have stresses substantially lower than this relationship would predict. Additionally, on unloading, these films show stress-temperature slopes not predicted by a simple dislocation model. The films were again measured after 100 Å of tungsten was applied to the surface of the gold films and allowed to oxidize. We found that the observed stresses are only minimally affected for films thicker than 1 micrometer. Thinner films were able to sustain much higher stresses, especially at elevated temperatures. This strengthening effect on thinner films is consistent with the shutting down of diffusion near the free surface of the film.

9:15 AM V2.3
ACTIVATION VOLUME FOR INELASTIC DEFORMATION IN POLYCRYSTALLINE Ag THIN FILMS. Mauro J. Kobrinsky 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 ($T < 200$ °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 rates of stress relaxation during isothermal annealing of thin films 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 volume are consistent with 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 the 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 V2.4
MECHANICAL PROPERTIES OF ELECTROPLATED COPPER THIN FILMS. R. Spolenak[1], C. Volkert[1,2], K. Takahashi[1], S. Fiorillo[1], J. Miner[1], and W.L. Brown[1]; [1]Bell Labs, Lucent Technologies, Murray Hill, NJ; [2]Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

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 criterium. In the case of aluminum studied by Venkatraman and Bravman, anodic oxidation was used 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 change in grain size. Stress-temperature curves were measured for two sets of electroplated copper films by a laser scanning wafer curvature 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 stress was found to increase with decreasing film thickness for both sets of samples, as anticipated. The set that had been annealed after 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 bimodal grain size distribution originating from the recrystallization process at room temperature.

9:45 AM V2.5
HALL-PETCH HARDENING IN PULSED LASER DEPOSITED COPPER AND NICKEL THIN FILMS. J.A. Knapp, D.M. Follstaedt, J.C. Banks and S.M. Myers, Sandia National Laboratories, Albuquerque, NM.

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 $H = H_0 + Kd^{-1/2}$, where d is the grain diameter and H_0 and K are constants. The limit of applicability 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 5-20nm. To test the Hall-Petch relationship using a new method of sample preparation, we formed thin films of both Ni and Cu on silica using pulsed laser deposition (PLD). The PLD technique can produce very small grains, and transmission electron microscopy shows that the sizes in layers deposited at room temperature were 6-20 nm and 20-45 nm, respectively, for Ni and Cu. Ultra-low-load indentation testing combined with an analysis based on finite-element modeling was then used to evaluate the mechanical properties of the layers. This analysis accurately determines the intrinsic yield stress, Young's modulus, and hardness of the layers from the indentation data, separating the properties of the thin films from those of the substrate. For room temperature deposited films, the measured hardnesses for Ni and Cu were 11.1 ± 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-AC04-94AL85000.

10:30 AM *V2.6
HYDROGEN INDUCED PLASTIC DEFORMATION OF THIN FILMS. A. Pundt[1], U. Laudahn[1], U.v. Hüelsen[2], U. Geyer[2], T. Wagner[3], M. Getzlaff[4], M. Bode[4], R. Wiesendanger[4], R. Kirchheim[1]; [1]Institut für Materialphysik, Universität Göettingen, Göettingen, GERMANY; [2]Erstes Physikalisches Institut, Universität Göettingen, Göettingen, GERMANY; [3]Institut für Werkstoffwissenschaft, MPI für Metallforschung, Stuttgart, GERMANY; [4]Institut für Angewandte Physik, Universität Hamburg, Hamburg, GERMANY.

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 Nb-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. Out-of-plane strain and in-plane stresses during electrolytic hydrogen 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 H-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 the dislocation lines were observed on the surface of a Gd (0001) film by using Scanning Tunneling Microscopy. Additional surface pattern were observed that can be correlated with emitted dislocation loops.
* U. Laudahn, A. Pundt, M. Bicker, U. v. Huelsen, U. Geyer, T. Wagner, R. Kirchheim, to be published in J. Alloys Compounds 1999.

11:00 AM V2.7
EFFECTS OF UNDERLAYER COMPLIANCE ON FLOW STRESS IN Al THIN FILMS. Seungmin Hyun, 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 various thicknesses of polyimide. The polyimide underlayer were deposited by spin coating, then thermally cured. Thickness was controlled by varying the amount of N-Methyl-2-pyrrolidone (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 $1\mu m$. The influence of underlayer thickness and compliance on the flow stresses of the Al thin films has been determined. The results are compared to predictions based on image dislocation forces in the adjoining layers.

11:15 AM V2.8
PLASTICITY IN Cu THIN FILMS. Volker Weihnacht, Winfried Brückner, Institute of Solid State and Materials Research Dresden, GERMANY.

A detailed study about the plastic behavior of thin Cu films with different thickness on oxidized Si substrates is reported. The investigations focused on stress measurements by wafer-curvature technique (WCT) in a home-made apparatus which allows bending experiments additionally to thermal cycling. By this novel technique, external strains up to 0.8% could be applied to Cu films on Si stripes. By measuring the course of stress by WCT after relief of bending stress, information about the strength and stress relaxation could be obtained at different temperatures. Besides stress measurements, a complex study of microstructure by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and x-ray diffraction has been done. Film stresses between 400 MPa (for 1000 nm Cu) and 550 MPa (for 200 nm Cu) were found after one thermal cycle up to 520°C. In the bending experiments it turned out that up to a theoretical bending stress (assuming elastic behavior) of 800 MPa in the Cu film only a little amount of plastic strain left after relief in all cases. In the TEM studies a strong parallel alignment of dislocations at the film/substrate interface was observed in some grains. Moreover, hints for mechanical twinning were found, indicated by tips of twin lenses ending in the grain and terraces on the grain surfaces (observed by SEM) with similar dimensions as twin lamellas found by TEM plan-view observations. Finally, a model of dislocation interaction is proposed which explains both the high film strength and the small amount of plastic strain after bending by a reversible strain hardening mechanism.

11:30 AM V2.9
STRAIN RELAXATION IN THIN FILMS: THE EFFECT OF DISLOCATION BLOCKING. Peter J. Goodhew, Univ of Liverpool, Dept of Engineering, Liverpool, UK.

The relaxation of strained layers frequently occurs by the glide of threading dislocations. From very early on in the relaxation process, gliding dislocations will be forced to intersect a number of prior dislocations with almost-perpendicular line directions and their progress may be blocked. This effect has been widely reported in semiconductor films, and there is some experimental evidence that it is reduced when layers are grown on vicinal substrates. This implies that the blocking is sensitively dependent on the dislocation configuration and in particular on the dislocation line directions. In this paper the interactions between gliding threading dislocations and the perpendicular or nearly-perpendicular dislocation in their path are modelled quantitatively. The differences arising from different initial dislocation configurations and different predominant line directions are found to be small. Strain relaxation, at least in its early stages, should be virtually independent of the initial dislocation configuration.

11:45 AM V2.10
MEASUREMENT OF THIN FILM MECHANICAL PROPERTIES BY MICROBEAM BENDING. Jeffrey Florando, Dept of Materials Science and Engineering, Stanford Univ, Stanford, CA; Qing Ma, Harry Fujimoto, Intel Corp, Santa Clara, CA; Ruth Schwaiger, Oliver Kraft, Max-Plank Institut fur Metallforschung, Stuttgart, GERMANY; William D. Nix, Dept of Materials Science and Engineering, Stanford Univ, Stanford, CA.

There is a continuing need for the development of new techniques for studying the mechanical properties of thin films on substrates. Recently a new microbeam bending technique utilizing triangular beams was introduced. The technique is similar to previous work done on microbeam bending, except that triangular shaped silicon microbeams, created by micromachining, are used. For this geometry, the film on top of the beam deforms uniformly when the beams are deflected, unlike the standard rectangular geometry in which the bending is concentrated at the support. The yielding behavior of the film can be modeled to a Ramburg-Osgood constitutive law, which is then used to predict the stress-strain relation for the film while attached to its substrate. Utilizing this technique, the microstructure-mechanical property relations for Al and Cu thin films were studied. Specifically, we examined the effects of film thickness, grain size, heat treatment, and cyclic loading on the stress-strain behavior of the films.

SESSION V3: EPITAXY, DEPOSITION PARAMETERS, MICROSTRUCTURE AND STRESSES

Chairs: Paul R. Besser and Huajian Gao
Tuesday Afternoon, November 30, 1999
Room 306 (H)

1:30 PM *V3.1
SILICIDE INDUCED MECHANICAL STRESS IN Si: WHAT ARE THE CONSEQUENCES FOR MOS-TECHNOLOGY. Karen Maex, IMEC, Leuven, BELGIUM, also at INSYS, Katholieke Universiteit, Leuven, BELGIUM.

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 Si 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 devices.

2:00 PM V3.2
EXCESS VACANCY GENERATION BY SILICIDE FORMATION IN Si. R.J. Jaccodine, 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 defect perturbations will influence motion of diffusions that are in the adjacent viscinity. $TiSi_2$ 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 silicates 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, Eric P. Kvam, Purdue University, Materials Engineering, W. Lafayette, IN; En-Hsing Chen, Jerry M. Woodall, Yale University, Electrical Engineering Department, New Haven, CT.

Mismatch stress relaxation mechanisms in bilayer films of (In,Al)As on InAs on GaP have been examined. Initial edge (90°) 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 later introduction of glissile (60°) 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 relaxed InAs, exhibits a different mechanism of misfit dislocation introduction. Threading dislocations move by climb, directly introducing sessile edge dislocations at the buried interface. It is believed this is the first time that this mechanism has been observed.

2:30 PM V3.4
$Si_{1-x}Ge_x$/Si HETEROEPITAXY ON PATTERNED SUBSTRATES. Cengiz S. Ozkan, Applied Micro Circuits Corporation, Process Development Division, San Diego, CA.

Graded $Si_{1-x}Ge_x$ heteroepitaxial thin films grown by low pressure chemical vapor deposition on patterned Si substrates were investigated with regard to strain relaxation and defect nucleation, poly-$Si_{1-x}Ge_x$/epi-$Si_{1-x}Ge_x$ interface structure and the dependence of the growth process characteristics on the substrate crystallographic orientation. The heterostructures were characterized by using transmission electron microscopy for morphology and defects, and by secondary ion mass spectrometry for in-depth chemical profiling. While $Si_{1-x}Ge_x$ grows epitaxially on single crystal Si regions over the substrate, poly-$Si_{1-x}Ge_x$ growth occurs on dielectric regions such as SiO_2 and Si_3N_4. Microtwins and threading dislocations were observed at the interface between poly-$Si_{1-x}Ge_x$ and epi-$Si_{1-x}Ge_x$, which can be detrimental to the electrical characteristics of devices. Film growth over single crystal Si regions can be strongly effected if the surface of the region is non-planar. 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 UNIQUELY ORIENTED SIGE/SI EPITAXIAL LAYERS. Morgan Ware, Robert Nemanich, 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 layers. The 4 percent lattice mismatch between the Si and Ge face centered cubic structure allows thin epitaxial layers of

Si(1-x)Ge(x) to be grown compresively strained to the lattice spacing of the Si substrate for low x. This strain can be relaxed by two main methods. One is to simply grow the layers thick enough so that the strain overcomes the interfacial bonding forces and defects form letting the layer assume its natural spacing. The other is to grow to a thickness where the layer is 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 angles, $\theta =$ (0, 10, 22) degrees. Using Raman spectroscopy we have seen shifts of up to 5 wavenumbers between the relaxed and unrelaxed states in the Si-Si mode of the epilayers. The annealed samples showed considerable surface roughening as seen in AFM regardless of their state of strain before annealing.

3:30 PM V3.6
COHERENT AND INCOHERENT PLASTIC RELAXATION IN III-V HETEROSTRUCTURES. Andrè Rocher, Etienne Snoeck, 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 epitaxial 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 which induces a coherent and periodic relaxation mechanism creating the well organized misfit dislocations network. The GaAs/InP system has been grown at 450°C in order to obtain both an uniform thickness and good crystalline quality of the GaAs epilayer. Some nm above the interface, the GaAs layer becomes well relaxed by a network of randomly distributed partial and 60° dislocation segments with a limited length. At low growth temperature, the plastic relaxation appears directly at the growth front when the individual adatoms take a position different from the ideal pseudomorphic one. In this case, the relaxation mechanism is incoherent.

3:45 PM V3.7
TENSILE STRESS GENERATION, FRACTURE, AND DISLOCATIONS IN III-NITRIDES. J.A. Floro, S. Hearne, J. Han, D.M. Follstaedt, S.R. Lee, J. Figiel, J.A. Hunter, Sandia National Laboratories, Albuquerque, NM; E. Chason, Brown University, Div. of Engineering, Providence, RI; I. S.T. Tsong, Arizona State University, Dept. of Physics and Astronomy, Tempe, AZ.

Typical III-nitride semiconductor thin films have complex microstructures that could be characterized either as lousy epitaxy, or as terrific (highly oriented) polycrystals. We have used real-time stress measurement during chemical vapor deposition of GaN on sapphire and AlGaN on GaN, combined with ex situ structural characterization, to correlate the evolution of stress and microstructure. 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 hollow-core dislocations. We also examined stress evolution in AlGaN alloy 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 low density mud-crack network combined with a high density of interfacial misfit dislocations between the cracks. We speculate that cracks are necessary in order to permit facile introduction of glissile dislocations, 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-ACO4-94AL85000.

4:00 PM V3.8
STRESS EFFECTS IN THE OXIDATION OF PLANAR SiO_2 THIN FILMS. T.J. Delph and R.J. Jaccodine, Depts. of Mechanical Engineering and Materials Science, Lehigh Univ., Bethlehem, PA.

The oxidation kinetics of SiO_2 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 SiO_2 occupies approximately 2.3 times as much volume as an atom of Si. Because almost all of the expansion brought about by this volume change takes place normal to the plane of oxidation, it is commonly thought that planar oxidation serves as a sort of a 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 marked curvatures, indicating the presence of fairly large in-plane stresses induced by the oxidation process. Delph (*J. Appl. Phys.* **6**, 574, 1998) has interpeted 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 Kobeda and Irene (*J. Vac. Sci. Tech B* **6**, 574, 1988) have yielded a value for this 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. Delph and Lin have recently analyzed the effects of these stresses upon oxidant diffusion in planar films. One of the interesting consequences of this study is that oxidant diffusivities in SiO_2 derived from the parabolic coefficient in the Deal-Grove model may be as much as 16% in error as a consequence of in-plane stress effects. Recently, Mihalyi, Jaccodine, and Delph (*Appl. Phys. Lett.* **74**, 1981, 1999) have examined the growth of very thin oxides upon silicon strips loaded in four-point bending. Under these conditions, the oxide film is subjected to an externally imposed in-plane stress of constant magnitude. It was found that compressive in-plane stresses 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 reaction. 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. Krzanowski, S. Koutzaki, Mechanical Engineering Dept., University of New Hampshire, Durham, NH; J. Nainaparampil, Systran Corp., Dayton, OH; J.S. Zabinski, Wright Laboratories/Materials Directorate, Wright-Patterson AFB, Dayton OH.

Hard carbide coatings are widely used to improve wear resistance and reduce friction 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 carbides 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 in the Ti-Si-C system TiC and SiC are essentially insoluble. Coatings in these systems were fabricated by co-sputtering from carbide targets, allowing a complete range of film compositions to be obtained in each system. The films were deposited on Si and sapphire substrates at temperatures ranging from room temperature to 650C. 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 Si exhibited a stronger (111) orientation in comparison to films deposited on sapphire. Mo was found to be soluble in TiC up to about 80% Mo, and between 80-90% Mo 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 2-3 times compared to TiC alone. The optimal composition for hardness enhancement is near 10% SiC in TiC. Additional experiments are underway to explore the tribological properties of these films.

4:30 PM V3.10
EFFECT OF ANNEALING ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF TiN-TiB_2 FILMS. Anita Madan, Richard A. Hoffmann, Jian-Sheng Wang, Keith Martin and Michael A. Graham Advanced Coating Technology Group Northwestern University, Evanston, IL.

Mechanism-based models predict that TiN-TiB_2 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-TiB_2 composite films. The films were sputter deposited on sapphire substrates in a dual-opposed-cathode unbalanced-magnetron sputtering system using TiN and TiB_2 ceramic targets. The variable speed rotating substrate holder alternatively faced the two targets. The volume of TiN fraction was varied from 20% to 80% 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 nanoindentation. Preliminary experiments indicate that the hardness of the annealed 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.

4:45 PM V3.11
THE DIRECT CORRELATION BETWEEN ISLAND COALSECENCE AND TENSILE STRESS GENERATION DURING POLYCRYSTALLINE Ag FILM DEPOSITION. S.J. Hearne, J.A. Floro, J. Hunter, Sandia National Laboratories, Albuquerque, NM; E. Chason, Div. of Engineering, Brown University, Providence, RI; I.S.T. Tsong, Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ.

The tensile stress generation in evaporated metallic thin films growing in the Volmer-Weber mode is frequently associated with coalescence of discrete islands to form nascent grain boundaries. We have performed careful in situ stress measurements during UHV deposition of Ag films on SiO_2, 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 lead to stress generation. We will argue that this represents unconstrained boundary formation where lack of steric 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 zipping 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 stess generation will also be discussed.

SESSION V4: POSTER SESSION
Chairs: Paul R. Besser 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. Mitra[1], A. Madan[2], R. Hoffman[2] and J.R. Weertman[1]. [1]Department of Materials Science and Engineering, Northwestern University, Evanson, IL. [2]Advanced Coating Technology Group, Northwestern University, Evanston, IL.

Al-Ti multilayered films were deposited by magnetron sputtering of Al and Ti targets on Si (100) and NaCl substrates. The substrates were alternately passed under Al and Ti to obtain the desired multilayers. The bi-layer thickness was 16 nm with Ti constituting 12% of the total thickness. The films (1.7 μm thick) were annealed at 400°C (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_3Ti 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_3Ti 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-Al_3Ti composite structure. X-ray and electron diffraction analyses showed that Al_3Ti possessed the DO_{22} structure. Nanoindentor hardness values of as-deposited and annealed films (on Si substrates) was higher than those of pure Al or Ti films. The hardness decreased 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-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_3Ti 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.

V4.2
HARDNESS AND ELASTIC MODULUS MEASUREMENTS OF AlN AND TiN SUB-MICRON THIN FILMS USING THE CONTINUOUS STIFFNESS MEASUREMENT TECHNIQUE WITH FEM ANALYSIS. Thomas Rawdanowicz, Jag Sankar, NSF CAMSS, Dept of Mech Engineering, NC A & T State Univ, Greensboro, NC; J. Narayan, Vijay Godbole, NSF CAMSS, Dept of Materials Science and Engineering, NC State Univ, Raleigh, NC.

The hardnesses and elastic moduli of aluminum nitride (AlN) and titanium nitride (TiN) sub-micron thin films pulsed laser deposited (PLD) on silicon (111) were measured using nanoindentation based on a continuous stiffness measurement (CSM) technique. Thin film thicknesses, based on profile measurements of simultaneously grown step samples, are 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 wurzite 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 neglible substrate induced artifacts. Hardnesses of these AlN and TiN thin films 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
STRAIN RELAXATION AND MOSAIC STRUCTURE IN $Si_{0.7}Ge_{0.3}$ EPILAYERS GROWN ON Si(001) SUBSTRATES. J.H. Li, Physics Department, University of Houston, Houston, TX and Institute of Physics, Chinese Academy of Sciences, Beijing, CHINA.

X-ray double- and triple-axis diffractometry have been employed to study the strain relaxation and the mosaic structures in molecular-beam epitaxy grown $Si_{0.7}Ge_{0.3}$ epilayers on Si(001) substrates with a low-temperature buffer. The thickness of the $Si_{0.7}Ge_{0.3}$ layers ranges from 800 to 5000 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 structures. This indicates that at early stages of strain relaxation, the films contain mosaic structures laterally separated by perfect regions. This occurs because the strain field of a misfit dislocation 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 increase 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 co-existence of the perfect regions and distorted regions in the film is given as ρd=1 with ρ being the linear dislocation density and d the film 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
RAMAN SPECTROSCOPIC STUDY OF STRESS AND DISORDER IN SURFACTANT-MEDIATED MBE GROWN Ge(211)/Si(211). G. Brill, 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 4.3% lattice mismatch between Ge and Si, Ge is known to grow via the Stranski-Krastanov growth mode (2D followed by 3D) unless the surface free energy of the growing layer is suitably altered by a surfactant. Many groups have shown that by depositing 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 mode is altered significantly by saturating the Si 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 nucleated 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.

V4.5
ROOM TEMPERATURE DEPOSITION OF SILICON OXYNINRIDE FILMS WITH LOW STRESS USING A SPUTTERING-TYPE ECR PLASMA. Dawei Gao, Katsuhiko Furukawa, Hiroshi Nakashima, *Junsi Gao, *Junli Wang and *Katsunori Muraoka, Advanced Science and Technology Center for Cooperative Research, Kyushu University, Kasuga, Fukuoka, JAPAN.

*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, JAPAN.

Moisture penetration is known to be the main factor which influences the lifetime of organic electroluminescence (EL) devices. Hence, a passivation layer is indispensable for protecting the organic EL cell from moisture. In organic EL device fabrication, passivation layers 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 oxynitride (SiON) films were deposited at a room temperature using a sputtering-type ECR plasma system. SiON films were deposited as a function of flow rate ratio of O_2 to N_2 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 plasmas and to a silicon 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 etch rate, electrical resistance, and stress. The structural properties of the deposited films were investigated using FTIR and XPS. Also the adsorption 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 O_2 to N_2. High electrical resistance, high density and low stress oxynitride films could be formed at 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 SiO_2 and SiN films. In addition, the SiON film showed low stress and high electrical 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.

V4.6
VISCOUS FLOW IN DOPED AMORPHOUS Si AND PURE AMORPHOUS Se THIN FILMS. Jennifer A. Mullin, Frans Spaepen, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA.

Stress relaxation by Newtonian viscous flow was observed in sputter-deposited, doped amorphous Si and evaporated amorphous Se 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. Photo-effects on the viscosity of a-Se are being explored.

V4.7
PREFERRED ORITNTATION CONTROL OF PLATINUM THIN FILMS DEPOSITED BY DC MAGNETRON SPUTTERING USING Ar/N_2 GAS MIXTURES. Dong-Su Lee, Dong-Yeon Park, Hyun-Jung Woo, Jowoong Ha, INOSTEK, Inc., Seoul National University, Seoul, KOREA; Euijoon 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, a strongly (001)-oriented lead-zirconate-titanate (PZT) thin film is known to have a superior pyroelectric property. One way of controlling the preferred orientation of the oxide films is to controlling the preferred orientation of the bottom electrodes on which they are grown. It is highly likely that the strongly (001)-oriented PZT films may be grown on (200)-oriented Pt films. However, face-centered-cubic Pt films normally grows in (111)-textured films. Recently, we reported that the highly (200)-textured Pt films could be obtained by DC magnetron sputtering using Ar/O_2 gas mixture [1]. It was claimed that the changes in thin film stress with the incorporation of oxygen in the Pt films were responsible for the partial amorphization of Pt films. The selected seed Pt crystallites with (200) orientation grew in a controlled fashion during high-temperature annealing to form highly (200)-textured Pt film [2]. However, for some applications, the added oxygen tends to oxidize the underlying device structures. Instead, Ar/N_2 gas mixtures were used during Pt sputtering. It was found that the preferred orientation Pt films was similarly controlled by seed selection through amorphization and controlled grain growth (SSAG) as proposed in the previous study [2]. We will discuss the effects of various deposition parameters such as nitrogen contents, substrate temperature, annealing temperature, deposition pressure, etc., on the orientation, microstructure, and stress of the Pt films, and compare the results with those using Ar/O_2 gas mixtures. [1] M.H. Kim, et al., Changes in preferred orientation of Pt thin films deposited by a DC magnetron sputtering using Ar/O_2 gas mixture, J. Mater. Res. 14, 1255 (1999). [2] M.-H. Kim, et al.,Highly (200)-oriented Pt films on SiO_2/Si substrates by seed selection through amorphization and controlled grain growth, J. Mater. Res.14, 634 (1999).

V4.8
PROPERTIES OF Al-OVERLAYERS ON A TiO_2 (RUTILE) SURFACE: IN SITU STRESS MEASUREMENT. P. Oberhauser and R. Abermann, Inst. of Physical Chemistry, University of Innsbruck, AUSTRIA.

The chemical and microstructural properties of a surface have a strong influence on the growth mode and the morphology of a film evaporated onto this interface. Changes in the growth stress - measured in situ by a cantilever beam technique - of thin titanium films evaporated under UHV-conditions are used to monitor the respective properties of the substrate surface. The starting substrate film used in this study was a quasi single crystalline TiO_2-film (d=50 nm) prepared by reactive evaporation of titanium in an oxygen atmosphere and subsequent annealing (20 min, 400°C). The stress vs. thickness curve of titanium deposited on this substrate is interpreted to indicate epitaxial growth. Aluminum overlayers have been used to chemically modify the TiO_2-surface. The thickness of the Al-overlayers was increased from submonolayer range to 50 nm. The experiments show that thin Al-layers become oxidized, while the TiO_2-substrate is reduced (L.S. Dake and R.J. Lad, Surface Science 289 (1993) 297). The resulting Al-oxide overlayer is amorphous, and the single crystalline surface structure of TiO_2 is totally lost. At intermediate Al-film thicknesses the interface consists of a mixture of oxidized and metallic aluminum, while it is metallic at high thickness. These changes in the interface properties are clearly reflected in the growth stress of the Ti-film deposited at 120°C on the different substrates. The stress vs. thickness curves for the Ti-film indicate a transition from epitaxial growth on the highly ordered (uncovered) TiO_2-interface to polycrystalline film growth on the amorphous Al-oxide- and Al-interfaces. It will be shown that the Ti-growth stress is also affected by the surface geometry of the Al-overlayer surface.

V4.9
RELATION BETWEEN MACRO- AND MICROSTRESS IN THIN METALLIC LAYERS. Léon J. Seijbel, Rob Delhez, Delft University of Technology, Laboratory of Materials Science, Delft, NETHERLANDS.

Thin metallic or ceramic layers that are applied for protective purposes almost invariably contain very high, internal stresses. These stresses play an important role in the quality of the coating for its intended purpose, and may even lead to premature failure of the layer. However, when the conditions are favorable, the internal stresses may relax -usually by the motion of dislocations- so that the layer will not fail. We present the experimental determination of such stress behavior in thin metal layers by X-ray diffraction methods. This implies the measurement of macro-stress and strain (from the diffraction-line position as a function of specimen tilt) and the measurement of micro-stress and strain (from the diffraction-line broadening). Various models for the determination of the macrostress exist. These models have boundary conditions varying from constant stress (Reuss) to constant strain (Voigt) in all crystallites. We use a parameter that gives an indication for the amount of preservation of strain or stress. The microstress is related to the dislocation density in the layer. We calculate from the strain fields from dislocations the diffraction line broadening and compare it to the measurements. As an example we measure thin Ni layers (order 500 nm) sputter deposited on a Si wafer. The initial stress can be as high as 1.5 GPa. By temperature treatments the stress (both macro and micro) will be relaxed. XRD-measurements will be compared with line-broadening calculations and TEM experiments.

V4.10
INFLUENCE OF THE DEPOSITION PARAMETERS ON THE ELECTRICAL AND MECHANICAL PROPERTIES OF PHYSICALLY VAPOR DEPOSITED IRIDIUM AND RHODIUM THIN FILMS. Ilan Golecki and Margaret Eagan, AlliedSignal, Inc., Morristown, 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 actual values of these properties in thin films depend on the microstructures and purity levels, which are determined by the synthesis method and conditions. In the present study, Ir and Rh thin films have been deposited in high vacuum on chromium-coated (100-300 A Cr), thermally-oxidized (∼5000 A silicon dioxide), four inch diameter silicon substrates by means of electron-gun physical vapor deposition. We will describe the variation of electrical sheet resistance and film stress of the Ir and Rh films as functions of the substrate temperature during deposition, the deposition rate and the film thickness.

V4.11
MICROSTRUCTURAL EVOLUTION IN COPPER FILMS UNDERGOING LASER PULSING AT HIGH PRESSURES.
R. Jakkaraju, C.D. Dobson, A.L. Greer, Dept of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK.

The current technologies for fabricating multilevel metallization are likely to be inadequate on account of the high aspect ratio via and contact holes in future sub-0.25 μm device geometries. We have developed a novel process involving high pressure and laser pulsing 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 oxidised Si substrate with an array of via 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 pulsing along with an application of a pressure of 70 MPa. The microstructural evolution of the film has been investigated by X-ray diffraction, focused ion beam microscopy (FIB) and cross-sectional TEM. The FIB images of the film show a chequer-board pattern of grains duplicating the square pattern of via holes underneath. We explain the chequer-board 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 films. Even though the as-deposited films have a $< 111 >$ fibre 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 TEMPORARY SRENGTHENING OF THIN Al FILMS.
J.P. Lokker, G.C.A.M. Janssen, DIMES, Delft University of Technology, Dept of Applied Physics, Delft, THE NETHERLANDS; S. Radelaar, Netherlands Institute of Metals Research, Delft, THE NETHERLANDS.

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 one can measure stresses in alloyed thin films as a function of temperature by the wafer curvature technique. In this paper we present the influence of thermal history on the mechanical behaviour of thin alloyed films during cooling. It is found that an isothermal hold period at a temperature between 473 K and 573 K leads to considerable stress relaxation. Upon further cooling however, strengthening of AlCu thin films is observed. The strengthening is defined as the maximum difference in stress measured during cooling with and without an isothermal hold period. The strengthening is only temporary and upon further cooling the stress returns to the stress-temperature curve obtained without an isothermal hold period. It is found that the strengthening slightly increases with the hold period, increases with decreasing isothermal hold temperature and increases with the Cu concentration. To investigate the relevant importance of diffusion and solubility we also studied AlNi and AlCr thin films. Ni in aluminum combines a relative high mobility with virtual no solubility while Cr in Al combines a relative low mobility with a somewhat higher solubility. In these alloys the strengthening is not as clear as in AlCu or sometimes not observed at all. The trends observed for AlCu point to the formation of Cottrell atmospheres of copper near dislocations during the isothermal hold which in turn are responsible for the increase in yield point. From the observation for AlNi and AlCr it is concluded that both an appreciate solubility as well as an relative high solubility are needed for temporary strengthening.

V4.13
IN SITU STUDY OF DISLOCATION BEHAVIOR IN COLUMNAR Al THIN FILM ON Si SUBSTRATE.
Charles W. Allen, Materials Science Division, Argonne National Laboratory, Argonne, IL; Herbert Schroeder, Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, Jülich, GERMANY; Jon M. Hiller, Madison Area Technical College, Madison, WI.

In situ transmission electron microscopy (300kV) 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 are established with lateral sizes ranging from 2 to 20μm. On rapid cooling (3-5°C/sec) from 500°C, dislocations first appear at 360-380°C, quickly multiplying and forming complex arrays on further cooling. Damage effects associated with a 300kV incident 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 material 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.
Deok-kee Kim[1], William D. Nix[2], Eduard Arzt[3], Michael Deal[1], James D. Plummer[1]; [1]Center for Integrated Systems, [2]Department of Materials Science and Engineering, Stanford University, Stanford, CA, [3]Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY.

Thermal hillocks in sputter-deposited Al films have been studied as a part of a broad study of stress-induced diffusional processes in Al. The Al films were annealed for 2 hours at 450°C in forming gas. The median grain size of the as-deposited Al film was 69nm; the grain size increased to 90nm after annealing. Trace amounts of the impurities Ti, W, and O were incorporated 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/SiO_2 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 form of hillock formation by modifying boundary conditions of Chaudhari's hillock model. Our model describes hillock formation by diffusion of Al atoms from 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 can be 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 NANOINDENTATION.
Eiji Kusano, Yoshihiro Sawahira, Naoto Kikuchi, Akira Kinbara, Kanazawa Institute of Technology, Matto, JAPAN.

Effects of metal underlayer thickness on plastic and elastic energies dissipated during the stylus loading process in nanoindentation have been investigated for the film with a layer system of a hard toplayer of TiN (Young's modulus of 250-300GPa) and a soft underlayer of Cu (Young's modulus of 130-140GPa). The bilayer films were deposited on aluminosilicate glass substrate by dc magnetron sputtering using an ultra-high vacuum apparatus. The thickness of the TiN toplayer was 250nm, while that of the Cu underlayer was varied from 0 to 500nm. Nanoindentation measurements were carried out by using a three faced pyramidal diamond stylus for maximum loads of 2.94, 4.90, and 6.86mN. The nanoindentation depth was $<$50 % of the TiN layer thickness for all stylus loads. It is found that the microhardness decreased 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 thickness. The increase in the plastic energy was more remarkable at a higher stylus load. The ratio of energy dissipated to that applied in the nanoindentation process 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 behaviors can be explained by the difference in the moduli of the two materials.

V4.16
SURFACE MODIFICATIONS DUE TO HYDROGEN INDUCED PLASTIC DEFORMATION OF GD FILMS.
A. Pundt[1], M. Getzlaff[2], M. Bode[2], R. Wiesendanger[2], R. Kirchheim[1]; [1]Institut für Materialphysik, Universität Göettingen, Göettingen, 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 Nb-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 change of the surface morphology of an epitaxial Gd (0001) film 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. Two different features were found: disc-shaped islands and slope 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 GdH_2-precipitation is expected and therefore is attributed to a subsequent emission of extrinsic dislocation loops. The slope field is attributed to a glide 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 the growth of the GdH_2 regions 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 Wang[1], Richard L. Edwards[2] and Kevin J.Hemker[1,3]; [1]Department of Materials Science and Engineering, [2]Applied Physics Laboratory, [3]Department 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 plain-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 plain-strain modulus that is slightly lower than the literature values for a {111} textured film. The Von-Mises equivalent 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-STRAIN RELATIONSHIPS BE OBTAINED FROM INDENTATION CURVES USING CONICAL AND PYRAMIDAL INDENTERS? Yang-Tse Cheng, General Motors R&D Center, Warren, MI; Che-Min 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.

[1] Y.-T. Cheng, and C.-M. Cheng, Int. J. Solids Structures 36, 1231 (1999).
[2] Y.-T. Cheng, and C.-M. Cheng, J. Appl. Phys. 84, 1284 (1998).

V4.19

MEASUREMENT OF RESIDUAL STRESSES BY LOAD AND DEPTH SENSING SPHERICAL INDENTATION. Bostjan Taljat, STEEL Group,Treviso, ITALY; George M. Phar, Univ of Tennessee, Dept of Materials Science and Engineering, Knoxville, TN, and Oak Ridge National Laboratory, Metals 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/ideal-plastic 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 wide variety of metals and ceramics. Elastic-ideal-plastic materials were considered, with the residual stress levels varied from zero up to the yield stress. All three indentation regimes - elastic, elastic-plastic, and plastic - were examined, with emphasis given to the elastic and the early part of the elastic-plastic regimes, 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 from measurements of the 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.

Research sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., and through the SHaRE Program under contract DE-AC05-76OR00033 between the U.S. Department of Energy and Oak Ridge Associated Universities.

V4.20

A METHODOLOGY FOR THE CALIBRATION OF SPHERICAL INDENTERS. J. Gregory Swadener, George M. Pharr, University of Tennessee, Dept. of Materials Science & Engr., Knoxville, TN and Oak Ridge National Laboratory, Metals 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 nonlinear compliance in the testing machine. The calibration of spherical indenters is further complicated, because asperities on the indenter and surface roughness add to the uncertainty in locating the surface of the sample. In addition, spherical indenters are generally made of anisotropic single crystals, and the calculation of their elastic responses must include their anisotropy. To address these difficulties, a methodology has been developed for the calibration 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 synthetic ruby 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-AC05-96OR22464 with Lockheed Martin Energy Research Corp. This research was conducted using the Shared Research Equipment User Facilities at ORNL.

V4.21

THE IMPLICATIONS OF ENERGETIC AND KINETIC SURFACE INSTABILITY FOR A STRESS MEASURMENT TECHNIQUE. H.H. Yu, Z.Suo, Princeton Univ., Princeton, NJ.

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 has 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 state, 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. Hurtado and H. Tan, Evolution of surface-roughness spectrum caused by stress in nanometer-scale chemical etching. Submitted for publication. [2] W. Barvosa-Carter and M.J. Aziz, L.J. Gray and T. Kaplan, 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 AND HEATING PROCESS. Mengcheng Lu, Chunangad S. Sriram, 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 an 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 films first develop a biaxial tensile stress due to solidification and initial drying. At the final stage of drying where the drying stress vanishes, dilation of the film recreates the porosity of the wet gel state, reducing the residual stress to zero. The surfactant templated films also experience a low drying stress due to the influence of the surfactant on surface tension and extent of siloxane condensation. Aerogel films develops a large tensile or compressive stress at intermediate temperature (depending on which surface modification reagent is used to modify the siloxane 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.

V4.23
MECHANICAL CHARACTERIZATION OF SURFACES BY NANOTRIBOLOGICAL MEASUREMENTS OF SLIDING AND ABRASIVE TERMS. Susan Enders, Peter Grau, 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 behaviour becomes 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 single asperity 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 behaviour of the friction of tribological pairs with different mechanical properties in the ultra-low load region. 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 coefficient for 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 pairs. By taking into consideration various theories about the adhesion of solids an estimation of its influence on nanoscratching tests can also be given.

SESSION V5/MM10: JOINT SESSION:
THIN FILMS FOR APPLICATIONS IN MEMS
Chair: Richard Vinci
Wednesday Morning, December 1, 1999
Room 306 (H)

8:30 AM V5.1/MM10.1
WAFER SCALE TESTING OF MEMS STRUCTURAL FILMS. Brian J. Gally, C. Cameron Abnet, Stuart Brown, Exponent, Inc., Natick, MA.

Biaxial 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 bulge testing method. An array of 0.5 μm thick silicon-rich silicon-nitride membranes were 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 extracted 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 biaxial modulus and residual stress of the films to be mapped over the wafer surface with a sensitivity of better than $\pm 5\%$. Results from wafers fabricated at three foundries are presented and compared.

8:45 AM V5.2/MM10.2
FATIGUE BEHAVIOR OF THIN SILVER FILMS INVESTIGATED BY DYNAMIC MICROBEAM DEFLECTION. R. Schwaiger, O. Kraft, Max-Planck-Institut f. Metallforschung, and Institut f. Metallkunde, University of Stuttgart, GERMANY.

It is now 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 higher 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. Sudden decreases 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 microscopic techniques were applied to characterize the microstructure of 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 V5.3/MM10.3
BENDING RESPONSE OF A 100 NANOMETER THICK FREE STANDING ALUMINUM CANTILEVER BEAM. M.A. Haque and T.A. Saif, 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 99.99% 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 micron by point loading. Two cycles of loading and unloading were carried out . The experiment was observed in-situ under 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 report a bending test of a 100 nanometer thick free standing film showing a significantly large yield stress compared to its bulk counterpart.

9:15 AM V5.4/MM10.4
FILM STRESS INFLUENCE OF BILAYER METALLIZATION ON THE STURCTURE OF RF MEMS SWITCHES. R.E. Strawser, R. Cortez, Air Force Research Laboratory; M.J. O'Keefe, University of Missouri-Rolla, Dept. of Metallurgical Engineering; K.D. Leedy, J.L. Ebel, Air Force Research Laboratory, Wright-Patterson AFB, 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 microwave/ millimeter wave applications. In this study, cantilever and bridge microswitches were fabricated on GaAs substrates using bilayers of titanium and gold metallization in with the total thickness was held constant at 1.5 μm but the thickness of gold varied from 0.5 μm to 1.5 μm. The lengths of the cantilevers were varied from 300 to 500 μm and the bridge lengths were varied from 600 to 800 μm while the cantilever and bridge beam width was fixed at 50 μm. The switch metals were deposited via either e-beam evaporation or electroplating. Qualitative comparisons of the topography and the resulting 'stiffness' of the released switches were made using focused ion beam/scanning electron microscopy. Thin film stress measurements using laser reflectometry of the various ratios of titanium/gold metallization films deposited on bare wafers revealed an increasing intrinsic tensile stress as the gold ratio increased. The upward deflection of the gold dominated cantilever beams corroborated this trend of increased tensile stress. A discussion of the observed microswitch structure within the context of the measured film stresses will be presented and recommendations for future metallization studies will be made.

9:30 AM V5.5/MM10.5
STUDY OF STRESS IN Pt/PZT/Pt/Ta ON SILICON WAFER FOR FABRICATION OF PZT MEMS PRESSURE SENSOR. Eugene Zakar, Madan Dubey, Brett Piekarski, Richard Piekarz, John Conrad, and Robert Widuta, US Army Research Lab, Sensors and Electron Devices Directorate, Adelphi, MD.

Stress was studied in piezoelectric PZT ($Pb(Zr,Ti)O_3$) films using a commercial stress analyzer which measures warpage with a laser-reflection system. PECVD oxide, nitride, and oxide/nitride/ oxide (47 to 255 nm thick films) were deposited at 250°C on silicon (100) wafers (3-inch diameter). The oxide and nitride films were heat treated in furnace of the stress analyzer under nitrogen from RT-860°C-RT at a rate of 25 and 30°C/min with in-situ stress measurement. For as deposited oxide layers (90 and 255 nm thick), measured stress was compressive (-351 and -579 MPa respectively), and changed from -579 to -186 MPa after heat treatment. Similarly stress for (47 and 165 nm thick) nitride was compressive (-78 and -90 MPa respectively) which changed from -78 to +520 MPa after heat treatment. Ta (20 nm) and Pt (170 nm) were sputter deposited on the above oxide and nitride films at 100°C with (Ta-160/Pt-240) nm/min deposition rate for bottom electrodes. The average stress in as deposited Ta/Pt on nitride was -570 MPa, which changed to average $+3.5 \times 10^6$ MPa after RTA annealing at 700°C for 60 sec. Stress due to the (Ta/Pt) films, deposited on 90 and 255-nm thick oxide, were -576 and -785 MPa respectively. The RTA treatment further changed the stress from -576 to $+2.8 \times 10^6$ MPa and -785 to $+2.2 \times 10^6$ MPa. When (Ta/Pt) films were deposited on a sandwich of (Oxide-213/Nitride-203/Oxide-200 nm) films, the measured stress was -1089 MPa which changed to $+2.7 \times 10^6$ MPa after similar RTA treatment. Sol-gel deposited PZT thin (500-nm) film on Ta/Pt electrodes created an average +580 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. Heiko Hesemann[1], Peter Müllner[2], and Eduard Arzt[1]; [1]Max-Planck-Institut für Metallforschung and Institut für Metallkunde, Universität Stuttgart, Stuttgart, GERMANY; [2]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 thin films. 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 plane in both phases. The martensitic 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 repeatedly found in 3.0 μm thick films. In these films, the microstructure changes during cycling 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. Neither transformation nor texture change occur at 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 FILLERS. Haobin Luo, Bin Tang, Miriam Rafailovich and Jonathan Sokolov, NSF-MRSECs, Garcia Center for Polymers at Engineered Interfaces, Department of Materials Science & Engineering, State University of New York at Stony Brook, Stony Brook, NY; Hyun-Joong Kim, Division of Biological Resources and 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 slobs were molded and a layer 100nm thick of monodispersity PS (90K) or copolymer mixture of graft and block copolymer containing various fraction of carbon black and clay was spun coated on the surfaces. PS/PMMA, and PMMA/PMMA joint were then made. The Gc (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 decreased Gc 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. X. Xia, K.B. Yoder, L.E. Scriven, 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 a 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 Hysitron Triboscope combines nanoindentation testing and atomic force microscope (AFM) imaging. A humidity-controlled chamber has been recently designed for the in situ study of humidity 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 vol% and 5 vol% PVOH solution were tested under 10%, 50% and 70% relative humidity. Elastic moduli were calculated from unloading stiffness and contact area after nanometer scale petrations. 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 standard viscoelastic model has been found. The moduli obtained 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 PVNP with SDS surfactant courtesy of Dr. Brunt 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 nanomechanical 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 nanomechanical 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, change the abrasion mechanisms and the morphology of the abraded surface. Using the scratch technique, along with profilometry measurement across the scratches, we have been able to completely characterize the residual scratch morphology. Pile-up deformation and visco-plastic 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 METROLOGY OF 0.1 MICRON POLYMER FILMS. C.C. White and W L. Wu, 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 ultra-thin (<0.1 micron) polymer films have shown deviations from the assumed bulk behavior. The majority of these studies have employed ellipsometry to measure changes in the film thickness as a function of temperature. Good measures of the bulk glass transition temperature of polystyrene have been known for at least thirty years. Due to the small sample thickness, traditional techniques used to characterize the glass transition temperature are not applicable. New metrology is 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 ultra-thin films will be presented. The first of these techniques employs a viscosity sensitive fluorescent probe. The second technique uses twin 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.

11:30 AM V6.5
NANOMECHANICAL PROPERTIES OF THE THIN-FILM ORGANIC MATRIX IN MOLLUSC SHELL NACRE: A BIOMIMETIC MODEL. Jeffrey M. Sopp[1], Hanson Fong[1], Andrew Bleloch[2] and Mehmet Sarikaya[1]; [1]Materials Science and Engineering, University of Washington, Seattle WA, [2]Materials Dept, Cambridge University, Cambridge, UNITED KINGDOM.

Nanomechanical properties were determined from the organic matrix of a mollusc hard tissue using a nanomechanical testing instrument attached to an atomic force microscope (AFM). The inner section of red abalone (Haliotis refuscens) shell (nacre, or mother-of-pearl) has a brick and mortar microarchitecture with pseudo-hexagonal-shaped bricks made of aragonitic $CaCO_3$ platelets (0.25 micrometers thick, and 5 micrometers edge length) surrounded by a thin (5-25 nms thick) proteinaceous organic matrix. In addition to the details of the microstructure, mechanical properties of these biocomposite constituents need to be evaluated. When cleaved, nacre splits between the platelets resulting in surfaces covered with a thin (<10 nms) film of the organic matrix material. For the estimation of surface roughness and film thickness, cleaved nacre samples were imaged using AFM at scales approximating calculated contact 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 nanoindentation system was used to make indentations at 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 electrochemically etched to various semispherical-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 nanocomposite 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 POLYSILSESQUIOXANE NETWORKS. Bizhong Zhu, Dimitris E. Katsoulis, John R. Keryk, Central R&D, Dow Corning Corporation, Midland, MI; Frederick J. McGarry, Department of Materials Science and Engineering, M.I.T., Cambridge, MA.

Polysilsesquioxanes are used as interlayer insulating materials for microelectronics. However these materials are brittle, especially under tension caused by the thermal expansion mismatch and curing shrinkage. In this study the mechanical properties of several representative cured polysilsesquioxane 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/U10: 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
TRIBOCHEMISTRY OF ZDOL DECOMPOSITION WITH HYDROGENATED CARBON OVERCOATS. C. Singh Bhatia, IBM, San Jose, CA; Chao-Yuan Chen; Walton Fong; Changhong Jiang; David B. Bogy, University of California, Dept 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 hydrogenated (CH_x) carbon disks coated with ZDOL lubricant. The studies involved drag tests with uncoated and carbon-coated Al_2O_3-TiC sliders and thermal desorption 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 breakage of the backbone bonds to yield free-radical segments. Chain scission can occur by three mechanisms: (1) random degradation, (2) depolymerization, and (3)weak-link degradation. Our studies further support previous observations that catalytic reactions occurred at the endgroup functionals. The lower number of endgroup functionals for ZDOL with higher molecular weight reduces the possibility of the occurrence of catalytic reactions. Moreover, the ZDOL desorbed 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 chain decreases, the desorption energy needed to break the lubricants increases, resulting in higher desorption peak temperatures. In addition, the longer chain length of the higher molecular weight ZDOL causes higher degrees of crosslinking. The crosslinking restricts chain mobility and causes an increase in the desorption peak temperatures.In summary, the talk will discuss the lube degardation 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. Vlad Novotny, TeraStor Corporation, San Jose, CA; Boris Druz, Veeko Instruments, Inc., Plainview, NY.

First optical surface recording heads and disks represent an ideal system to study tribology of thin films in-situ with a high degree of 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 a signal, which monitors physical contacts between asperities 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 dependence 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 nanohardness of these films were 150 and 230 GPa, and 23 and 55 GPa for ion beam and cathodic arc films, respectively. An adequate agreement was been 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 AS THIN AS 6 NM OR LESS. T.W. Wu, IBM Almaden Research Center, San Jose, CA; T.W. Scharf, 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 (CNx) have been assessed by a micro-wear scan technique. These CNx coatings, with the 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/sec along the y-direction with a gradual increased load. Because of this reciprocating, ramped-loading and scanning combined testing 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, based on the first occurrence of coating 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 ~2nm regime. However, the 1nm thick CNx coating deviated from this 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, UK; R. Pastorelli, M.G. Beghi, C.E. Bottani, Dip di Ingegneria Nucleare, Politecnico di Milan, ITALY.

The determination of the elastic constants of thin, attached films is extremely difficult. The reduced Youngs modulus is often extracted as from nano-indentation tests used to measure hardness. Laser-induced surface acoustic waves (SAWs) can also be used. The difficulties of using nano-indentation 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 ta-C are found to be between 60 and 90 GPa. However, the Youngs modulus values derived by indentation are much more widely scattered, 400-1100 GPa. We show that Surface Brillouin Scattering (SBS), a SAW method, can for the first time determine all the isotropic elastic constants of hard-on-soft and soft-on-hard films, even less than 10 nm in thickness [1]. We find that the Youngs modulus, shear modulus and Poissons ratio of ta-C with a 88% sp3 fraction and 3.26 g/cm3 density are 757 GPa, 337 GPa and about 0.12 respectively. We find for ta-C:H with 70% sp3 and 30% hydrogen and 2.35 g/cm3 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 of ta-C is less than diamond, while the moduli of ta-C:H are considerably less than those of ta-C because of the weakening effect of C-H bonding.
[1]A C Ferrari, et al, submitted to App Phys Lett.

2:45 PM V7.5/U10.5
TENSILE PROPERTIES OF AMORPHOUS DIAMOND FILMS.
D.A. LaVan, J.P. Sullivan, T.A. Friedmann and C.I.H. Ashby, Sandia National Labs, Albuquerque, NM.

A computer-controlled Nanoindenter was used to test amorphous diamond samples in uniaxial tension by pulling laterally with a flat 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 other had a ring that was engaged with the tip of the Nanoindenter. 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 into the applied tensile force and frictional losses. 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 load-displacement data from those samples that failed in the gage section was converted to stress-strain curves using the specimen cross section and gage length dimensions verified by measuring against a standard in the SEM. 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.

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. Lucas, 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, real geometry. The evolution of shear stress under the indenter will be 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. Fries, 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 human joints, 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 wear surfaces by microwave plasma chemical vapor deposition (MPCVD) following MPCVD nitridation. Cobalt chrome often delaminates any deposited diamond film due to a high thermal expansion mismatch of 13.5 K^{-1} for cobalt chrome as opposed to only 1.13 K^{-1} for diamond. Additionally, cobalt chrome promotes the degradation of the growing diamond film into graphite, by absorption of carbon into the metal lattice. By nitriding the cobalt chrome through MPCVD prior to diamond deposition, a usable diamond film may be achieved. Since both nitridation and deposition will be performed by MPCVD, there is the possibility of merging the nitriding and deposition steps into a single process. We will also present experimental data on microcrystalline deposition as well as nitrogen-assisted 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 GRADIEND DIAMONDLIKE COATINGS. Q. Wei[1], A.K. Sharma[2], S. Yarmolenko[1], J. Sankar[1] and J. Narayan[2], NSF Center for Advanced Materials and Smart Structures. [1] Dept of Mechanical Engineering, McNair Hall, North Carolina A&T State University, Greensboro, NC, [2]Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Pure diamondlike carbon thin films largely bonded by four-fold coordination suffer from a large internal compressive stress that gives rise to serious adhesion problem. In this work, functionally gradient diamondlike carbon thin coatings were prepared by pulsed laser deposition in a high vacuum as an alternative approach to address the adhesion problem of diamondlike 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 400 nm in thickness. Nanoscale mechanical characterizations using Nanoindenter XP^R 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 SHIELDED ARC ION PLATING. Nobuhiro Tajima, Hiroki Saze, Hiroyuki Sugimura and Osamu Takai, Department of Materials Processing Engineering, Graduate School of Engineering, Nagoya University, Nagoya, JAPAN.

Hydrogen free amorphous carbon (a-C) and carbon nitride (a-C:N) were synthesized by means of shielded arc ion plating in which a shielding plate was inserted between a target and a substrate in order to reduce macroparticle deposition onto the substrate [1]. Thin films of a-C and a-C:N were prepared in an arc discharge plasma of argon or nitrogen gas, respectively, at a pressure of 1 Pa by using a graphite target as cathode. Mechanical properties of these films was studied in relation to substrate bias voltage with a nanoindenter. 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 wrear resistant. On the contrary, the hardness of the a-C:N 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-C:N films was comparable to or better than the a-C films.. In particular, the a-C:N film prepared at a bias of -300 V was so wear resistant that the film did not wear at all when rubbed with a diamond tip at a contact force of 20 μN. The presence of β-C_3N_4 like phase characterized by a N1s XPS peak at 400.5 eV has found to be crucial for wear resistance of the a-C:N films. [1] Y. Taki, T. Kitagawa and O. Takai, This Solid Films, 304 (1997) 183.

4:30 PM V7.10/U10.10
INTRINSIC STRESS MEASUREMENTS IN CVD DIAMOND FILMS. J.G. Kim, Hyundai Electronics Ltd., Ichon, KOREA; Jin Yu and Y.C. Sohn, KAIST, Dept of Materials Science and Engineering, Taejon, KOREA.

Diamond films were grown over the (100) Si substrate by the hot filament CVD method 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 CVD temperature was measured after removing the diamond layer using the reactive ion etching method. Results showed that the intrinsic stress in the film as 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 Rajamini, Janet Rankin, Rod Beresford, Brown University, 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 nitrides. 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
Chairs: Jerrold A. Floro and Thomas J. Wyrobek
Thursday Morning, December 2, 1999
Room 306 (H)

8:30 AM *V8.1
THE BRITTLE TO DUCTILE TRANSITION (BDT) IN ADHERED THIN FILMS. William W. Gerberich, A. Volinsky, N. Tymiak, Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN; and N.R. Moody, Sandia National Lab, Livermore, CA.

It has been long recognized that the BDT in bulk materials may be associated with enhanced plastic energy dissipation. This can be achieved by either changing the state of stress (plane strain to plane stress) or by raising the test temperature (lowering the yield stress). The situation is somewhat different in thin films where the BDT can be achieved by increasing film thickness or perhaps, even in a limited temperature range, by raising the test temperature. To study the latter we use a superlayer technique with a 1 μm tungsten film on top of thin copper films bonded to SiO_2/Si wafers. This involves indenting into the superlayer which stores and then releases large amounts of elastic 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 absorption would appear to be limited by film thickness, this relatively large value was unanticipated. 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. Is this associated 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;
- a 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 LIFT-OFF TEST: EXPERIMENTAL MODIFICATIONS FOR MULTIFILM SYSTEMS. Eric Liniger, Xiao Hu Liu, Jack C. Hay, 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 application of the technique to multi-film 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. Thus, cracks often run on the interface between the silicon and 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 on the interface of interest. Data suggests that a two-step preparation method yields clean delaminations on 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; Huajian Gao, Anna Vainchtein, 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 complicated geometry and many interfaces within the fracture process zone itself. Moreover, plastic flow in metal layers is often severely constrained by the surrounding structure, 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 investigate 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 produce the same work of adhesion and cohesive strength, the stress distributions they produce in the process zone differ. These differences raise the question of how many parameters are sufficient to characterize the cohesive nature of a material or interface. We compare our predicted variations in 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 Miura, Mechanical Engineering Research Laboratory, Hitachi, Ltd., Tsuchiura, JAPAN.

Highly integrated semiconductor devices and magnetoresistive heads are made up of layers of thin films, and the thickness of each film is gradually being reduced to within a few nanometers. Since atomic diffusion is especially active near the interfaces between films of different materials, it sometimes leads to delamination and voids, which cause the reliability of the devices to deteriorate. We therefore have developed a molecular-dynamics technique for analyzing the adhesion strength of the interfaces between thin films a few nanometers thick. This technique uses the extended Tersoff potential, which enables us to analyze the adhesion strength of metal/dielectric films as well as metal/metal films. The adhesive fracture energy is obtained as the difference between the total potential energy of the film-layered state and that of the film-separated state. This technique was applied to the analysis of peel strength of interfaces between ULSI-interconnect materials (Al and Cu) and diffusion-barrier materials (TiN and W). And we found that the adhesive fracture energy of the Al/TiN interface is about four times larger than that of the Al/W one. This result is consistent with the well-known fact that a TiN film is a good diffusion barrier between an Al interconnect film and a W plug in USLIs. On the other hand, the adhesive fracture energy of the Cu/TiN interface is about a half that of the Cu/W interface. The analysis results were confirmed by scratch testing and tape testing. We thus conclude that the molecular dynamics technique is effective for predicting adhesion strength of interfaces.

9:45 AM V8.5
APPLICATION OF BRIDGED INTERFACE FRACTURE MODEL TO LOW k / Cu INTERFACE CRACKS IN SEMICONDUCTOR PROCESS. Yusheng Feng, Motorola, Inc., Computational Technologies Lab, Austin, TX; Mikhail Perelmuter, Russian Academy of Science, Institute for Problems in Mechanics, Moscow, RUSSIA; Ting Tsui, AMD-Motorola Alliance, Austin, TX; Jeff Wetzel, SEMATECH, Austin, TX.

The demand for high performance microprocessors, microcontrollers and fast static memories has driven the semiconductor industry to explore new low k materials and Cu technology with applications to sub-0.25 micron interconnect. As a result, it poses many challenges to interconnect reliability and process integration. Interface cracks and delamination may occur during one of the silicon chip fabrication processes. Since polymeric materials are among the possibilities for low k insulators for the next generation multilevel interconnect, the use of classical Griffith fracture model may not be adequate to describe the end zone at the crack tip for polymer interfaces. In this presentation, we use a mechanical and mathematical model of the interface crack with bridged bonding in its end zones. The model assumes that distributed spring-like polymer bonds link crack surface in some zones starting from the crack tips. The sizes of these zones are not assumed to be negligibly small in comparison with the crack length. Using superposition method, the system of two singular-differential equations are formulated and solved to evaluate normal and shear bond stress tensor components in the end zone. The stress intensity factors at the crack tip are calculated by taking into account a compensating action of the bonds. Preliminary results show that the simulation agrees with the experimental data in terms of energy release rate Gc using both mELT (modified Edge Liftoff Test) and Four Point Flexure Adhesion Test.

10:30 AM V8.6
SUPERLAYER RESIDUAL STRESS EFFECT ON THE INDENTATION ADHESION MEASUREMENTS. Alex A. Volinsky, Neville R. Moody, William W. Gerberich, Univ. of Minnesota, MN.

Ductile thin film adhesion can be measured by means of the superlayer technique. A layer of a hard brittle material on top of the film of interest (superlayer) provides enough driving force for delamination and prevents severe plastic pile-up. Aluminum films of eight thicknesses between 40 nm and 3.2 microns were sputter deposited on top of the thermally oxidized silicone wafers with and without a 40 nm thin Cu adhesion-weakening layer. Two one micron thick W superlayers with 1 GPa compressive and 100 MPa tensile residual stresses were deposited on top of the Al films. The residual stress in the W superlayer was controlled by argon pressure in the sputtering chamber. Compressive stress in the superlayer prevents the indenter from going deeper into the film, on the other hand, it provides more energy for debonding. For a given load, films with the compressive stress superlayer produced larger blisters than those with a tensile stress superlayer. However, films with the tensile stress superlayer were susceptible to radial cracking up to the edge of a blister and showed higher load excursions on the load-displacement curves. Measured adhesion values for Al films on Si ranged from 1 to 12 J/m^2.

10:45 AM V8.7
MEASURING THIN FILM FRACTURE TOUGHNESS USING THE INDENTATION SINKING-IN EFFECT AND FOCUSED ION BEAM MILLING TECHNIQUES. Ting Y. Tsui, Young-Chang Joo, Advanced Micro Devices, Sunnyvale, CA.

A new experimental technique is developed to measure the fracture toughness of a hard nickel phosphate (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 generated by means of the indentation sinking-in effect. The effect creates a bending moment and tensile stress on the hard thin film near the indentation that promotes crack growth. The amount of crack tip blunting prior to the critical failure was measured from the FIB cross-sectioned micrographs. By using the crack tip opening displacement model (CTOD), the fracture toughness of the thin film was calculated. The results show the NiP thin film fracture toughness is $\sim$15MPa $m^{1/2}$. Finite element method (FEM) was used to understand the mode of mixity near the crack tip. The results indicate the crack tip mode of mixity is dominated by the Mode I opening provided the indentation is sufficiently far from the pre-crack.

11:00 AM V8.8
ON THE ROBUSTNESS OF SCRATCH TESTING FOR THIN FILMS: THE ISSUE OF TIP GEOMETRY FOR CRITICAL LOAD MEASUREMENT. Vincent Jardret, 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 shape, the fracture resistance of a surface can be characterized by the load required to create fracture damages. The scratch technique has demonstrated its ability to create these damage mechanisms and characterize the critical load for coatings failure. However, 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 1micron were used 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 INDIUM OXIDE THIN FILMS ON POLYMER SUBSTRATES. D.R. Cairns, S.M. Sachsman, D. Sparacin, R. Witt, G.P. Crawford and D.C. Paine, Brown University, Division of Engineering, Providence, RI.

The integration of ceramic thin films of tin doped indium oxide – a transparent conductor – with mechanically dissimilar polymeric substrates is an essential step in the development of light weight flat panel display systems. One widely touted application is the wearable flexible flat panel display but such devices will require materials systems that are mechanically robust with respect to repeated flexure, 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 polymeric substrates (polyethylene terepthalate, acrylic, pmma) materials loaded in uniaxial tension while monitoring the evolution of the thin film microstructure using in situ resistivity measurements and ex situ AFM and elecvtron microscopy. In one study we have monitored 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 propogate across the gauge length of the specimen. As a consequence, 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 80-atom bixbyite unit cell of indium oxide combined with the need to minimize the temperature seen by the polymer substrate means that thinner films tend to be amorphous (as established by GIAXD). The interplay of these observations with the mechanics of the indium oxide on polymer system will be discussed.

11:30 AM V8.10
STUDY OF CRACK PROPAGATION AT AN OXIDE/POLYMER INTERFACE UNDER VARYING LOADING CONDITIONS. Dimitrios Pantelidis, Jeffrey Snodgrass, Reiner Dauskardt and John

Bravman, Stanford University, Dept of Materials Science and Engineering, Stanford, CA.

We investigate the failure mode of the interface between a benzocyclobutene (BCB) polymer film and an oxidized silicon wafer under both cyclic and monotonic loading conditions. In all cases the interface fails cohesively and a polymer layer of nm scale thickness is left on the oxide surface after fracture. Analysis of the fracture surface though, using angle-resolved XPS, AFM and cross-sectional TEM, reveals that the thickness and morphology of the polymer layer left on the oxide is different for different loading modes. We correlate these crack path selection issues with microstructural and chemical mechanisms responsible for interface adhesion and mechanical behavior.

11:45 AM V8.11
DECOHESION, INTERFACIAL MORPHOLOGY AND THERMO-MECHANICAL PERFORMANCE OF THERMAL BARRIER COATINGS. Daniel R. Mumm, Harvard University, Division of Engineering and Applied Sciences, Cambridge, MA.

Ceramic thermal barrier coatings (TBC's) designed to protect metal components subjected to high-temperature, oxidizing atmospheres are susceptible to delamination and spalling. It has long been known that coating failures are: (a) associated with a thermally grown oxide (TGO) layer that forms during high temperature exposure, (b) motivated by residual stresses that develop due to mismatch between the TGO and the underlying bond coat, and (c) governed by the fracture characteristics of the TGO and the metal/oxide interface. However, a detailed mechanistic understanding of interfacial cracking, damage coalescence and spalling failure of TBC's is only now emerging. Recent studies have shown that morphological evolution of the TGO/bond coat interface plays a key role in interfacial decohesion. For a particular class of TBC materials, morphological evolution of the metal/oxide interface is closely tied to the bond coat chemistry. In particular, yttrium additions to the bond coat have a pronounced effect on interfacial morphology. High-resolution chemical and microstructural studies of yttrium-containing and yttrium-free materials, at various stages of evolution, elucidate the mechanisms responsible for the observed morphological evolution. Mechanical test methodologies, developed for quantitative studies of coating fracture and decohesion, have been implemented to study the effects of morphology on delamination and spalling. Results of the study suggest that the influence of yttrium on the morphological characteristics of the TGO/bond coat interface may be an important component of the much-discussed reactive element (RE) effect.

SESSION V9: RELIABILITY IN MICROELECTRONICS
Chairs: Karen Maex and Ralph Spolenak
Thursday Afternoon, December 2, 1999
Room 306 (H)

1:30 PM *V9.1
STRESS DEVELOPMENT IN DIELECTRIC THIN FILMS. Robert F. 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 silsesquioxane spin-on glass materials is considered, with particular emphasis on the development of the athermal and thermal stresses. Spin-on glasses are candidates for use as low dielectric-constant insulating materials in advanced microelectronic interconnection structures where great mechanical reliability is required during fabrication and in use. Attention is focused on the effects of residual tensile stresses on stress-corrosion cracking of spin-on glasses.

2:00 PM V9.2
ADSORPTION/DESORPTION PHENOMENA IN SILICATE GLASSES: MODELING & APPLICATION TO A SUB-MICRON BICMOS TECHNOLOGY. Thomas Hoffmann, Vincent Senez, ISEN-IEMN, UMR CNRS-8520, Dept of Process Simulation, Villeneuve d'Ascq, FRANCE; Philippe Le Duc, Philips-Components, Thin Films & Back-End Engineering, Caen, 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 reflowed at relatively low temperatures to help to planarize the underlying topography. However, the moisture resistance of highly doped oxides is reduced compared to thermal or undoped oxides and may deteriorate 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-4, 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 strains/stresses corresponding to the film volume increase (adsorption) or shrinkage (desorption). Experimental measurements giving the variation of stress in doped (PSG, BPSG) and undoped silicate 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, the large hysteresis observed for doped CVD oxides help to calibrate the water evaporation rate and 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 cracklings in SOG films during densification.

2:15 PM V9.3
MOLECULAR MECHANICS STUDY OF SURFACE STRESS IN SILICON OXIDE LAYER. Aruba Yamada, Seiichi Tamami, Akira Endou, Kazuo Teraishi, Momoji Kubo, Akira Miyamoto, Tohoku Univ., Dept. of Materials Chemistry, Sendai, JAPAN; Akiko N. Itakura and Masahiro Kitajima, 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 Itakura 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) method, and the calculated results have been compared with the 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 axis, beta and gamma angles of the super cell are fixed. In this model, the oxidation was assumed to be a layer-by-layer model. We made 0(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 stresses are observed in these calculations. These theoretical calculations correspond well to the experimental results.
[1] A.N. Itakura, T. Narushima and M. Kitajima, J.Trans. MRS-J. 24 (1999) (in press).
[2] C.J. Casewit, K.S. Colwell and A.K. Rappe, J. Am. Chem. Soc. 114, 10046 (1992).
[3] Cerius2 Version 3.5, MSI (1997).

2:30 PM V9.4
THE MECHANICAL PROPERTIES OF COMMON INTERLEVEL DIELECTRIC FILMS AND THEIR INFLUENCES ON ALUMINUM INTERNCONNECT RELIABILITY. Fen Chen, Baozhen Li, Timothy D. Sullivan, Clara Gonzalez, Christopher D. Muzzy, H.K. Lee, Mark D. Levy, IBM Microelectronics Division, Essex Junction, VT; Michael W. Dashiell, James Kolodzey, Electrical and Computer Engineering, University of Deleware, 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, appear to be a function of the SiO_2 underlayers. In this paper, nanoindentation, wafer curvature, and IR absorbance techniques have been used to study the mechanical properties of some of the most common interlevel dielectric SiO_2 films such as undoped silica glass using silane (SiH_4) precursor, undoped Silica glass using tetraethylorthosilicate (TEOS) precursor, borophosphosilicate glass (BPSG) and phosphosilicate glass (PSG) deposited by plasma-enchanced chemical vapor deposition (PECVD). Among the four common interlevel layers, BPSG shows the lowest as-deposited compressive stress and the lowest local Si-O-Si strain before annealing. The elastic modulus (E) and hardness (H) of the as-deposited and densified SiO_2 layers are measured by the nanoindentation technique. BPSG exhibits the smallest modules/hardness and a relatively small amount of moisture loss during annealing. The coefficients of thermal expansion (CTE) of the densified layers are estimated by temperature dependent wafer curvature measurements. The BPSG again shows the highest CTE which generates the smallest thermal stress due to the mismatch in the CTE between Al and SiO_2. Fourier transform infrared spectroscopy is used to obtain the chemical structures of all SiO_2 layers. The center frequency of the Si-O bond stretching vibration exhibits a linear dependence on total film stress. The shifts of Si-O peaks for all the SiO_2 layers also correlate well with the stress hysteresis obtained from wafer curvature measurements. The stress interactions between the various SiO_2 underlayers and the Al metal film are also investigated. The impact of the dielectric elastic properties on the interconnect reliability during thermal cycles is proposed. Our studies of the elastic properties of the different SiO_2 layers suggest that the BPSG is the most reliable interlevel dielectric layer for the control of extrusions and this result is directly consumed by our extrusion experiment on patterned wafers.

2:45 PM V9.5
STRESS, MICROSTRUCTURE AND TEMPERATURE STABILITY OF REACTIVE SPUTTER DEPOSITED Ta(N) THIN FILMS.
Kevin D. Leedy, Air Force Research Laboratory, Wright-Patterson AFB, OH; Matthew J. O'Keefe, University of Missouri-Rolla, Rolla, MO; John T. Grant, University of Dayton Research Institute, Dayton, OH.

Interest in tantalum nitride thin films for use as diffusion barriers in Cu-based microelectronic interconnects merits the study of tantalum nitride thin film properties as a function of deposition conditions and elevated temperature exposure. In this investigation, the influence of nitrogen content and post deposition annealing on the stress, microstructure and resistivity of Ta(N) films was analyzed. Ta(N) thin films were deposited by reactive dc magnetron sputtering of a Ta target in Ar/N_2 gas mixtures. With an increasing N_2 to Ar flow ratio, the as-deposited crystal structure of the films progressed from β-Ta to bcc Ta with N in solid solution to $TaN_{0.1}$ to Ta_2N and finally to TaN. The as-deposited Ta(N) stress, grain size and resistivity of these films were found to be strongly dependent on the phase(s) present. Film stress was measured $in-situ$ as a function of annealing temperature up to 650°C in flowing N_2 using a laser reflectometry system. Stress mechanisms associated with metastable phase transformations occurring at elevated temperatures were identified. Microstructural characterization using transmission electron microscopy and chemical analysis by x-ray photoelectron spectroscopy of the Ta(N) films were used to identify the as-deposited and transformed phases.

3:30 PM *V9.6
MATERIALS AND MECHANICAL BEHAVIOR ISSUES IN INTEGRATED CIRCUITS.
T. Marieb[1], H. Fujimoto[2], J. Lee[2], Q. Ma[2], L. Varner[2]; [1]Components Research, Intel Corporation, Hillsboro, OR; [2]Components Research, Intel Corporation, Santa Clara, CA.

The radical material changes occurring in the microelectronics industry will change the failure modes that are likely occur in service. Many new metrologies and models need to be developed to accurately estimate the lifetime of parts that are made from Cu interconnects with low k dielectrics. This talk will give an overview of the metrology techniques used in industry today to assess the thermomechanical stability of on die interconnect systems. The shortcomings of the current techniques, and the types of new techniques necessary will be discussed within the context of probable failure modes with the new materials being used.

4:00 PM V9.7
MECHANICAL STRESS MEASUREMENTS IN CONVENTIONAL AND DAMASCENE ALUMINUM INTERCONNECT LINES.
Paul R. Besser, AMD-Motorola Alliance Logic Technology, Austin, TX.

At the 0.22 or 0.18 μm technology node, the patterning of Al lines using deposition/subtractive etch or conventional processes becomes increasing difficult. Many IC manufacturers are investigating damascene fabrication methods as a replacement. Damascene methods have been shown to be via manufacturing processes for fabricating both Al and Cu interconnects. While mechanical stress generation 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 logic 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 methods. The effect of confinement associated with the damascene processing method will be shown to influence the strain and stress. In addition the effect of linewidth (from 0.5μm to 16 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 a strong function of ΔCTE, it is also strongly influenced by the constraints associated with the fabrication methodology. The implications for reliability will be discussed.

4:15 PM V9.8
PASSIVATED INTERCONNECT LINES: THERMOMECHANICAL ANALYSIS AND CURVATURE MEASUREMENTS.
Adam Wikstrom, Peter Gudmundson, Dept. of Solid Mechanics, Royal Institute of Technology (KTH), Stockholm, SWEDEN; Subra Suresh, 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 can be expressed (a) theoretically, for certain limiting 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 SiO_2 passivation. It is concluded that the presented approach is well suited for these material configurations.

4:30 PM V9.9
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 buildup, void formation in turn alters the stress state in the conductor lines. 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 continuum framework, we have quantified how voiding in interconnects relaxes the thermal stress. Contrary to what many researchers have used in estimating the total saturation void volume on the basis of differential thermal strain, the stress relaxation due to voiding is found to be a local phenomenon, bearing no direct relation with the global thermomechanical conditions of the interconnect. 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 a debonded patch 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 PM V9.10
ELECTROMIGRATION MODELING OF BLECH EXPERIMENT WITH COMPARISON TO RECENT EXPERIMENTAL DATA.
Zhineng Fan, M.A. Korhonen, and C.-Y. Li, Cornell Univ, Dept of Materials Science and Engineering, Ithaca, NY.

Finite element analysis is applied to simulate the electromigration in copper line/tungsten junction, which is a typical structure in Blech experiment adopted to measure the electromigration drift velocity by edge displacement. Because the specific resistivity of tungsten is higher than that of copper, the electric current crowds at the corner where the underlying tungsten bar connects to the edge of the copper line. Therefore, material in the corner is depleted faster than that in other places of the copper/tungsten interface. Our simulation reveals a stress that maybe high enough to crack the interface is also built up in the corner. The evolution of the line resistance under various current densities is calculated from our model and compared to the recent experiment results.

SESSION V10: POSTER SESSION
Chairs: Neville R. Moody and Edward Shaffer II
Thursday Evening, December 2, 1999
8:00 P.M.
Exhibition Hall D (H)

V10.1
FINITE ELEMENT ANALYSIS IN DESIGN OF A COATING SYSTEM FOR GLASS FORMING DIES AND TOOLS. D. Zhong, J.J. Moore, Colorado School of Mines, Advanced Coatings and Surface Engineering Laboratory, Golden, CO; S. Thiel, J. Disam, Schott Glas, 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 system for it. Stresses presented 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 thermal cycling between 450 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.

V10.2
ION IMPLANTATION AND MISFIT DISLOCATION FORMATION IN P/P+ SILICON. Petra Feichtinger, Hiroaki Fukuto, Rajinder Sandhu, Benjamin Poust, and Mark S. Goorsky, 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 periphery. This non-uniform dislocation distribution was utilized during subsequent implantation 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 misfits 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 multi-layer thin films.

V10.3
PHOTORELAXATION
AND THERMORELAXATION IN GeAsSe AMORPHOUS THIN FILMS. Steluta Adriana Dinca, National Institute for Research and Development in Microtechnologies, Dept. of Multidisciplinary Research, Bucharest, ROUMANIA; Mihai Popescu, National Institute of Materials Physics, Dept. of Materials Science, Bucharest-Magurele, ROUMANIA.

This work represents a study of the photorelaxation and thermorelaxation in $Ge_xAs_{40-x}Se_{60}$ 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. After UV irradiation it was observed a photoblanking effect for the samples with a low Ge concentration (x<20), and a photodarking effect for the samples with a high Ge concentration (x>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 GeAsSe 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 discussed in the terms of stress relaxation $Ge_xAs_{40-x}Se_{60}$ thin films. The structures remains amorphous, but the characteristic distance of medium range order decrease for x<20 and increase for x>20.

V10.4
ESSENTIAL PROPERTIES OF HARD COATINGS FOR LUBRICANT REDUCED MACHINING AND FORMING OPERATIONS. Erich Lugscheider, Otto Knotek, Cyrus Barimani, Kirsten Bobzin, Materials Science Institute, Werkstoffwissenschafften, Aachen 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 Ti-C-N coated inserts is several times greater than that of TiN coated ones. This is a result of the favourable thermophysical and tribological properties of Ti-C-N. The potential for tool protection of CrN is a result of the high ductility and low internal stresses of this coating material. CrN 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-C-N. Due to the carbon share in the coating an increasing hardness and a better wear behaviour in comparsion 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 coatings were tested in machining tests.

V10.5
STRESSES MEASUREMENT AND SIMULATION ON 3C-SiC THIN FILMS. C. Gourbeyre, C. Dubois, C. Malhaire, M. Le Berre, D. Barbier, Lab. Physique de la Matiere, INSA de Lyon, Villeurbanne, FRANCE; T. Chassagne, P. Aboughe-nze, Y. Monteil, Lab. Multimateriaux et Interfaces, Villeurbanne, FRANCE.

Although, 3C-SiC has outstanding physical properties to operate in harsh environments the devices 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. 3C-SiC epitaxy was carried out at 1350°C in a vertical cold wall reactor by atmospheric pressure Chemical Vapor Deposition, using the SiH4-C3H8-H2 system. The crystal growth procedure consisted in three steps. The first pregrowth step was the etching of the substrate with H2. The second step was the carbonization of the Si with C3H8. Then the third step was the CVD with a Si/C ratio of 0.3. Film stress measurements were performed using the bending plate method. The stress for 3 μm thick SiC layer is evaluated to be about 210-250 MPa with a concave 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 beetween 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 load-deflection measurements of free-standing diaphragms. This biaxial modulus is compared with the one obtained by nano-indentation. Finally the load-deflection measurements of suspended diaphragms are compared with the deflection behavior expected by Finite Element Modelling.

V10.6
NEAR-SURFACE DEFORMATION OF PAINTED POLY-PROPYLENE BLENDS. Houxiang Tang, David C. Martin, The University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI.

Quantitative estimates of the interfacial shear strength τ of coatings on substrates are important for a wide variety of technological applications. A tensile mechanical test was used to estimate τ 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: $\tau=1.337\sigma_{max}h_p/\bar{l}$ where σ_{max} is the tensile strength of the paint, h_p the paint thickness, and $\bar{l}$ the average crack spacing (Y. Letterier, et al, J. Adhesion, 44, 213-22 (1994)). The influence of sample 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 MICROLAMINATE COATINGS. R. Bahl, D. Patel, M. Vedawyas, 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 microlaminate coatings are made of many alternating layers of two hard materials, that, when combined in very thin layer 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-indention technique. Single layer of TiC and DLC and microlaminate DLC and TiC coatings with varying thickness were deposited on Si(100) substrates. Analysis of mechanical properties revealed that the hardness and modulus of properties of the multilayers are higher to monolithic coatings of either of the two constituent films. The cross-sectional TEM results were analyzed to understand the interfacial properties of these microlaminate coatings.

V10.8
DEPOSITION AND CHARACTERIZATION OF MECHANICAL PROPERTIES OF POLYMER THIN FILM COATINGS. D. Patel, M. Vedawyas 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 (7016) substrates by the pulsed laser deposition method. The films were deposited at room temperature to 400°C range. The structural and surface morphological properties have been evaluated using Fourier transform infra-red 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[1], Siu-Yue Tam[1], Randy Schunk[2] and C. Jeffrey Brinker[1,2], Advanced Materials Laboratory; [1]University of New Mexico/NSF Center for Micro-Engineering Materials, Albuquerque, NM, [2]Sandia 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 caused by 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 case of finding the value of the yield stress.

V10.10
ANISOTROPIC PLASTIC DEFORMATION VERSUS NEWTONIAN FLOW IN COLLOIDAL THIN FILMS DURING ION IRRADIATION. E. Snoeks[a], A. van Blaaderen[a,b], T. van Dillen[a], C. van Kats[b], M.L. Brongersma[a] and A. Polman[a]; [a]FOM-Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands, [b]Debye Institute, Utrecht University, THE NETHERLANDS.

Ion irradiation can be used to relax 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 stress. In this case an anisotropic stress generation process occurs that originates from the anisotropic shape of the thermal spike around the ion track at high electronic excitation density (> 2 keV/nm). When both the anisotropic stress generation and Newtonian plastic flow are active, a dynamic equilibrium sets in, leading to a compressive stress state. Using sensitive in-situ wafer-curvature measurements during 4 MeV Xe ion irradiation of SiO_2 thin films we have identified the various rate constants and parameters in these coupled processes, and unraveled their interplay.
Next, experiments were done on thin films of colloidal particles of SiO_2, ZnS, TiO_2 and Fe_2O_3 with diameters in the 100-2000 nm range. At low colloid density we find a dramatic anisotropic plastic 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 unconstrained, no stress builds 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
THE STRENGTH AND FRACTURE OF PASSIVE OXIDE FILMS ON METALS. M. Pang, D.E. Wilson, and D.F. Bahr, 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 are 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 nanoindentation 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. Ex situ film growth has been used to track the variations in average film properties. Observations of in situ film fracture measurements on single grains during film growth show the strength of the film remains 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 of the oxide has been observed 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. Valery Gurarie, School of Physics, MARC, University of Melbourne, Parkville, 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 films. The aim of the study is to 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 fragment size (crack density) as a function of the deposition temperature, thickness and thermal and mechanical properties of the films. Theoretical data on crack density are demonstrated to be in adequate 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 AMORPHOUS $Ge_{30}As_4S_{66}$ AND $Ge_{10}As_{20}Te_{70}$ THIN FILMS.

Nicolai D. Savchenko, Tatiana N. Shchurova, Uzhgorod Univ, Dept of Engineering, Uzhgorod, UKRAINE.

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 $Ge_{30}As_4S_{66}$ and $Ge_{10}As_{20}Te_{70}$ thin films has been studied. Thin films were deposited at different deposition conditions onto heated Ge, Si, GaAs, ZnSe, BaF_2, NaCl fused silica and K8 glass substrates of optical quality. Adhesion and shear strength measurements have been carried out by two-pin method. Adhesion strength determination has been conducted by the normal pull-off of the separated part of the film. Shear strength has been determined by the application of the external force (along 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 a cohesive nature.

V10.14
STRESS CORROSION CRACKING OF STAINLESS STEEL THIN FILMS. Robert Etien, Thomas M. Devine, University of California, Dept. of Materials Science and Mineral Engineering, Berkeley, CA.

Structural materials employed in applications that require long service lifetimes in corrosive environments, such as stainless steel cannisters of nuclear waste, must be resistant to the initiation of stress corrosion cracking. In particular, because of the ubiquitous nature of chloride ions, the cannisters 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 using thin film samples that ranged in thickness from 0.1 micron to 1.0 micron. The thin films were deposited onto substrates of silicon by pulse laser deposition. Using microfabrication techniques, a square shaped hole measuring 3mm x 3mm was introduced 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, thermal treatments resulted in tensile residual stresses in the stainless steel thin films. In the second method, the thin films were dynamically stressed in tension at selected loading rates by bulge testing. The samples strain was calculated from displacements measured by optical interferometery. The thin film samples were extremely sensitive to initiation of SCC with failures occurring within five seconds of exposure to 0.75M HCl. The samples were used to investigate the effects of microstructural and electrochemical variables on the initiation of SCC. Microstructural variables included grain size (minimum of 10 nm) and crystal structure (as deposited crystal structure was bcc, which was converted to fcc by heat treatment). Electrochemical variables included potential, pH and chloride ion activity.

V10.15
THREE-DIMENSIONAL MODELING OF FILM-EDGE-INDUCED STRESS IN SILICON DEVICE STRUCTURES FOR THE ANALYSIS OF LAYOUT-DEPENDENT DISLOCATION GENERATION. Igor V. Peidous, The University of the West Indies, Mona, JAMAICA; Konstantin V. Loiko, Dallas Semiconductor, Dallas, TX; Thomas Schuelke, Fraunhofer USA Resource Center, Ann Arbor, MI.

Many processes of microelectronic device fabrication initiate high mechanical stresses in device structures. Localized stresses at film edges are particularly large and, consequently, semiconductor substrates with patterned and embedded films often suffer of 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 assemblages were regularly detected in layout-specific regions at film edges. To find the cause of the observed premature onsets 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. Conventional approximation of concentrated forces was applied with modifications aiming to avoid a singularity problem and improve accuracy. Notwithstanding the simplifying assumptions used, the performed analysis of stresses in device structures was consistent with the experimental observations of layout-dependent dislocation generation. The area-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 Al 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 atomistically. Energetics as a function of stress were obtained for vacancy formation and migration, and interstitial migration. The bulk values calculated are in excellent agreement with experimental data. We will discuss the calculation methods and also discuss biaxial stress state effect. Finally, the impact on electromigration is pointed out based on the grain boundary results.

V10.17
MICRO FRICTION FORCE MEASUREMENT OF THIN FILMS PREPARED BY CO-SPUTTERING DEPOSITION TECHNOLOGY. M. Tosa, A. Kasahara, Y.S. Kim and K. Yoshihara, Natl Res Inst for Metals, Tsukuba, JAPAN.

Low friction coefficient 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 fiction coefficient accurately in-situ in the atmosphere controlling parameters of such surface conditions as contaminates layer, adsorbed layer and oxide layer by changing load and pressure. We have developed a microscale friction measurement system 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 nPa. The measurement was carried out on such materials as stainless steel, copper, boron nitride segregated copper film on steel, boron 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 supersaturated 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 c crystal plane of boron nitride parallel to the film surface. The result of 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 coefficient among them.

V10.18
MECHANICAL PROPERTIES AND ADHESION OF PZT THIN FILMS FOR MEMS. J.M. Jungk, 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; D.F. Bahr, 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 platinized silicon. The films have been tested using nanoindentation and scratching techniques. Three failure mechanisms in these films have been observed. Indentation induced delamination at the PZT - Pt interface occurs after the indenter tip is removed from the film when loads between 1 and 10 mN are applied to the sample; delamination while the indenter tip is in contact with the film occurs at approximately 10 mN , and scratch induced delaminations in front of the indenter tip at normal loads above 4 mN. At large loads, failure can be generated between the underlying sputtered oxide film and the silicon substrate. Since each of these failure modes has a different mechanics 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 micromachined 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.

V10.19

INTERDIFFUSION AND STRESS RELAXATION-RELATED ISSUES IN THE PROCESSING OF MULTILAYER METALLIC THIN FILMS FOR MEMS APPLICATIONS. G. Muralidharan, Victor Samper, Mnoon Yan Loke, Zhixiong Jiang and C.H. Tung, Institute of Microelectronics, Singapore, SINGAPORE.

Multilayer metallic thin films are used for a wide range of applications in the microelectronics industry. Examples span from the multilayer metallization used in Al-based or more recently Cu-based 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 micromachining- 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 excursion 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. The paper 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 presentation. Implications of such microstructural evolution for MEMS device processing, in particular, the actuator, will be highlighted.

V10.20

EFFECTS OF SEEDING OVER THE MICROSTRUCTURE AND STRESSES OF DIAMOND THIN FILMS. S. Gupta, G. Morell, R.S. Katiyar, 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 ellipsomtery (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 observed from the Raman band. The layered nature and microvoid fraction of these films were characterized by SE. We present correlations among seeding density, relative amount of non-sp3 phase, O/C ratio, grain size, internal stress, and total stress. These results help determine the best surface preparation for diamond film deposition. Authors wish to gratefully acknowledge the following NSF-DMR-9801759 US Grant for financial assistance.

V10.21

Transferred to V7.7/U10.7

V10.22

MICROMECHANICAL ANALYSIS OF RESIDUAL STRESS EFFECT IN CVD-PROCESSED DIAMOND WAFER. Jeung-hyun Jeong, Dongil Kwon, School of Materials Science and Engineering, Seoul National University, Seoul, SOUTH KOREA; Jae-Kap Lee, Wook-Seong Lee, Young-Joon Baik, Thin Film 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 (MPACVD), DC plasma (DCACVD) and hot filament assisted (HFACVD). However, high residual stress of diamond film induces bowing and through-thickness cracking in thick diamond wafer, and so 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. Quantification of intrinsic stress is limited due to two reasons. 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, other 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 calculated from the apparent curvature of substrate measured just after deposition and the creep curvature after diamond film removal. 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 CH_4 and H_2 by MPACVD. Based on the real measurement results and literature data, causes and effects of thickness dependence of intrinsic stress are discussed.

V10.23

RESIDUAL STRESSES IN MEMS STRUCTURES. Bhaskar S. Majumdar, UES, Inc./AFRL Materials Directorate; William J. Cowan, 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 composite 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 poly1, poly2, poly1+poly2, poly2+Au, and poly1+poly2+Au beams of thickness between 0.5 - 3 micrometers, where the poly's refer to polysilicon with different amounts of dopant. Beam sizes ranged from slender beams with large length-to-width ratios, 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 also is an athermal 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 anneal out. In order to de-couple 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 beams, and possible methods to reduce the residual stresses will be discussed.

V10.24

STRESS AND STRESS RELAXATION STUDY OF SPUTTERED PZT THIN FILMS FOR MICROSYSTEMS APPLICATIONS. Emmanuel Defaÿ, Christophe Malhaire, Christiane Dubois, Daniel Barbier, 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 as they are known to 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 stresses were 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 (180 μm Si + 0,66 μm thermal SiO_2) 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 (400°C, 30s, Ar). A 1 μm thick PZT layer was RF-magnetron sputtered and crystallized by a RTA (700°, 30s, Air). The as-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 and were correlated to the different phases of the PZT 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 were obtained by Secondary Ion Mass Spectrometry (SIMS). This time-dependent stress relaxation was then correlated to a lead and oxygen migration across the PZT layer.

SESSION V11: NANOINDENTATION AND ADVANCED TESTING TECHNIQUES

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

8:30 AM *V11.1

A SIMPLE MODEL FOR PILE-UP DURING INDENTATION BY A RIGID CONE. Haitao Song, Rice University, Dept of Materials Science, Houston, TX; George M. Pharr, The University of Tennessee, Dept of Materials Science & Engr. 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 nanoindentation data analysis procedures. A simple model is presented which can be used to predict the amount of pile-up in elastic-perfectly-plastic materials indented by a rigid cone. The model essentially provides a 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-displacement data 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 V11.2

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 storage of 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 dislocations. 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 V11.3

NANOINDENTATION EXPERIMENTS ON MONOCRYSTALLINE AND POLYCRYSTALLINE METAL FILMS ON SUBSTRATES: EFFECTS OF FILM THICKNESS AND CRYSTALLOGRAPHIC ORIENTATION. A. Gouldstone, 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 different thicknesses 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 influenced by the indenter tip radius. Both single-crystalline and polycrystalline metal films, 300 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 load-controlled 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 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 V11.4

FINITE ELEMENT AND ANALYTICAL MODELING OF NANOINDENTATION - RESULTS OF W FILM ON SAPPHIRE AND Al SUBSTRATES. Ranjana Saha and William D. Nix, 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 developed in recent years. W films with thickness varying from 0.5 micrometers to 2.0 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 (FEM) 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 hardnesses were then compared with experiment and significant deviations were observed. These differences can be explained by the inability of the Oliver-Pharr analysis of the experimental data to account for pile-up and sink-in effects. Analytical modeling of the elastic modulus was also attempted by using King's modification of an equation suggested by Doerner and Nix. We also examined the correction to the Sneddon solution proposed by Hay and Pharr.

9:45 AM V11.5

DETERMINING ELASTIC MODULUS AND HARDNESS FROM THE WORK OF INDENTATION USING CONICAL AND PYRAMIDAL INDENTERS. Yang-Tse Cheng, General Motors R&D Center, Warren, MI; Che-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).

10:30 AM V11.6

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.Wahl, 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 ultra-small 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 $\sim$0.1 N/m, which is sufficient to detect long-range surface forces and locate the surface of compliant materials. With this technique we have measured the mechanical response of silicon surface in four different regimes, the pre-contact, apparent contact, elastic contact and the elasto-plastic contact. We also present a novel quantitative 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.
Tong-Yi Zhang, Long-Qing Chen, Yan-Jing Su and Cai-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 be handle with. The microbridge testing is conducted with a load and displacement sensing nanoindenter system equipped with a microwedge probe. The problem of large deflection of the microbridge is solved analytically and numerically. The relationship of load-deflection is a function of the residual stress, the Young's modulus and the sample geometry. Fitting an experimentally 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 entirely 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. Kohl, M. Weller, E. Arzt, Max-Planck-Institut fuer Metallforschung, Stuttgart, GERMANY.

The elastic and anelastic properties of unpassivated copper thin films were studied by mechanical spectroscopy. Specimens with dimensions of 50x5x0.5 mm^3 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 eigenvibrations. 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 resonance-frequency give information on the temperature variation of Young's modulus and the adhesion between film and substrate.
The aim of the presented 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. Maris, 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 ALUMINIUM INTERCONNECTS USING CONVERGENT BEAM ELECTRON DIFFRACTION (CBED). Stephan Kramer and Joachim Mayer, 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-to-grain strain variation or the strain development during electromigration. Convergent beam electron diffraction (CBED) makes it possible to measure the lattice parameter with high spatial resolution (10-100 nm) 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 are 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 to 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 standard 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. Nobumichi Tamura, J.-S. Chung, G.E. Ice, B.C. Larson, J.D. Budai, and J.Z. Tischler, Oak Ridge National Laboratory, Oak Ridge, TN; W.P. Lowe, Howard University, Washington DC.

The availability of high brilliance 3rd generation synchrotron sources and recent advances in x-ray 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 sphere 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-AC05-96OR22464 with Lockheed Martin Energy Research Corp. N. Tamura and J.-S. Chung are supported under the ORNL Postdoctoral Research Associates Program administered jointly by ORNL and ORISE. 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.