SYMPOSIUM O

Thin Films–Stresses and Mechanical Properties XI

March 28 - April 1, 2005

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* Invited paper

TUTORIAL

Stresses at the Micro- and Nanoscale–Novel Testing and Characterization Techniques
Monday March 28, 2005
1:30 PM - 5:00 PM
Room 2022 (Moscone West)

The tutorial will consist of two major sections: measuring residual stresses in thin films and small volumes, and measuring the mechanical properties of thin films. The overall goal of the tutorial is to provide a basic understanding of the major techniques and tools used to perform these measurements. The instructors expect to provide enough information so that students, as well as experts in the field, will be able to directly compare advantages and drawbacks of all the tools and techniques described.

1. Measuring Stresses in Thin Films and Small Volumes
    (a) Substrate Curvature Technique (Chason Method)
    (b) Bulge testing
    (c) Diffraction Methods
    (d) Optical Spectroscopy Techniques to Measure Residual Stresses
2. Measuring the Mechanical Properties of Thin Films with a Special Focus on Nanoindentation
    (a) Review of Standard Instrumented Indentation Testing
    (b) Advanced Analyses of Nanoindentation Data
    (c) Commercially Available Instrumented-Indentation Tools
    (d) Scratch Testing
    (e) Novel Test Methods

Instructors:
Ralph Spolenak, ETH-Hönggerberg, Switzerland
Thomas Buchheit, Sandia National Laboratories

SESSION O1: Elasticity in Thin Films
Chair: Kazuki Takashima
Tuesday Morning, March 29, 2005
Room 2022 (Moscone West)

8:30 AM *O1.1
Advanced Resonant-Ultrasound Spectroscopy for Studying Anisotropic Elastic Constants of Thin Films. Hirotsugu Ogi, Graduate School of Engineering Science, Osaka University, Osaka, Japan.

This paper presents an advanced resonant-ultrasound-spectroscopy (RUS) method to determine the elastic constants Cij of thin films. Deposited thin films usually exhibit elastic anisotropy between the film-growth direction and in-plane direction, and they show five independent elastic constants. Because all of film Cij affect the mechanical resonance frequencies of a film/substrate layer specimen, resonance frequencies allows one to determine the film Cij inversely. Accurate resonance-frequency measurements are achieved by developing a piezoelectric tripod with needle-like transducers. Mode identification is unambiguously made by measuring displacement-amplitude distributions on the resonated specimen surface by laser-Doppler interferometry. We applied our technique to copper thin films, CVD diamond thin films, and Co/Pt superlattice thin films. They show elastic anisotropy and the Cij smaller than those of bulks. Micromechanics calculations suggest presence of incohesive bonded regions. Co/Pt superlattice thin films with various Co-Pt layer wavelengths were deposited on monocrystal silicon substrates by an ultrahigh-vacuum-evaporation method, keeping the volume fractions of the Co and Pt layers unchanged. Their perpendicular magnetic anisotropy ranged between -0.2 and 5 MJ/m3. Their hexagonal-symmetry elastic constants correlate with the magnetic anisotropy; higher perpendicular magnetic anisotropy causes larger in-plane elastic moduli and smaller out-of-plane moduli. Large elastic strains in the Co and Pt layers caused by their large lattice misfit explain this correlation through lattice anharmonicity and magnetostriction effect.

9:00 AM O1.2
Elastic Constants and Incohesive Grain Bonds of Nanocrystalline CVD-Diamond Thin Films: Resonant Ultrasound Spectroscopy and Micromechanics Calculation. Hirotsugu Ogi[1], Nobutomo Nakamura[1], Hiroshi Tanei[1], Ryuji Ikeda[2,3], Takemoto Mikio[3] and Masahiko Hirao[1]; [1]Graduate School of Engineering Scinece, Osaka University, Osaka, Japan; [2]Asahi Diamond Ind Co Ltd, Chiba, Japan; [3]Mechanical Engineering, Aoyama Gakuin University, Kanagawa, Japan.

Nanocrystalline diamond films show remarkable properties such as high thermal conductivity, low dielectric constant, and excellent hardness. Besides, they show provide nano-scale grain size and surface roughness to contribute to applications for optical devices and electron field emitters for flat panel displays. Few reports, however, appear studying elastic constants because of the difficulty of the measurement. Polycrystalline thin films usually show elastic anisotropy between out-of-plane and in-plane directions because of columnar structure, texture, residual stress, and local incohesive bonds. Then, they show transverse elastic isotropy with five independent elastic moduli. We develop an advanced resonance-ultrasound-spectroscopy technique to determine the independent elastic constants of nanocrystalline CVD-diamond thin films. They are deposited on monocrystal silicon substrates by the hot-filament methane/nitrogen CVD method. Mechanical free-vibration resonance frequencies of the film/substrate specimen depend on the dimensions, mass densities, and all of the elastic constants of the film and substrate. Thus, high-accuracy measurement of the resonance frequencies allows us to determine the elastic constants of the film inversely. We developed a piezoelectric tripod with needle-like transducers to measure the resonance frequencies with accuracy better than 10-5. Identification of resonance modes, which is an important key for successful determination of elastic constants, is achieved by measuring the displacement distribution on the vibrating-specimen surface with laser-Doppler interferometry. The elastic constants of nanocrystalline diamond films are smaller than those of microcrystalline CVD diamond films and bulk diamond. We attribute the compliant thin films to the presence of incohesive bonds at grain boundaries. A micromechanics model consistently explains this observation and estimates the volume fraction of defects.

9:15 AM O1.3
Mechanical Properties and Size Effect in Nanometric W/Cu Multilayers. Pascale Villain, Damien Faurie, Pierre-Olivier Renault, Eric Le Bourhis, Philippe Goudeau and Frederic Badawi; LMP, SP2MI, University of Poitiers - CNRS, Futuroscope Chasseneuil, France.

Recent numerical simulations have already shown that reducing the characteristic length scale (thickness or diameter) of a crystal with different shape (film or wire) down to a few nm leads to elastic modulus softening [1]. In fact, surfaces contribution becomes preponderant in nano-sized crystals yielding deviations from the average elastic behavior of the material. Moreover, the mechanical properties are known to differ from those expected from the bulk state. W/Cu multilayers with different period ranging from 24 down to 3 nm have been prepared by ion beam sputtering and characterized using x-ray reflectometry, x-ray diffraction, instrumented indentation and energy dispersive analysis in a Scanning electron microscope. The elastic behavior of W sub layers has been analyzed using a new method combining X-ray diffraction and tensile testing [2]. A decrease of the Young modulus is already observed when reducing the period thickness down to 3 nm. In addition, EXAFS measurements indicate that surface alloying may occur in tungsten sub layers for the lowest periods. A possible correlation between these two features is discussed. Furthermore, cracks initiation in the films was generated under the larger applied tensile stresses and under nano- and micro-indentation. The behavior was observed to depend on the period of these multilayers as well. The overall obtained results are commented in view of the previous ones. [1] Villain P., Beauchamp P., Badawi K.F., Goudeau P., Renault P.O., Atomistic calculation of size effects on elastic coefficients in nanometer-sized tungsten layers and wires, Scripta Materiala 50 (9) (2004) 1247-1251. [2] Badawi K.F., Villain P., Goudeau P., Renault P.-O., Measuring thin film and multilayer elastic constants by coupling in situ tensile testing with x-ray diffraction, Applied Physics Letters 80 (25) (2002) 4705-4707.

9:30 AM O1.4
Elasticity and Coalescence in Thin Metallic Films. Nail R. Chamsoutdinov and Amarante Bottger; Materials Science, TU Delft, Delft, Netherlands.

The results of a combined theoretical and experimental study on elasticity in nano-crystalline metallic films are presented. On the basis of energy considerations the effect of the geometry of grains and voids on elastic properties and stresses in these materials is investigated. Both free-standing films and films on a substrate are analyzed. The model considers the equilibrium between strain energy and energy of inter-granular interaction due to coalescence. The resulting analytical expressions for stress and the film's effective Young modulus contain geometrical parameters such as grain size, distribution of voids and material constants like the bulk Young's modulus and surface energy. For films on substrates, the stress depends on the volume of coalesced voids, while the effective Young's modulus is affected only by the density of voids with dimensions close to some critical value, which depends on the film's morphology. Free-standing films exhibit somewhat different behavior depending on the distribution of voids. Special attention is paid to investigate the limitations of the model. Experiments on elasticity and stresses in thin nano-crystalline Fe films (with grain size less than 100 nm) are performed and an excellent agreement with the predictions of the model is found. The available published experimental results on elasticity in other metallic thin films are also described well by the model.

9:45 AM O1.5

Improvement of the Elastic Modulus of Micromachined Structures using Carbon Nanotubes. Nicolas Duarte[1], Prasoon Joshi[1], Abhijat Goyal[1], Paul Sunal[2], Awnish Gupta[3], Srinivas Tadigadapa[1] and Peter Ecklund[3]; [1]Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania; [2]Engineering Science and Mechanics, The Pennsylvania State University, University Park, Pennsylvania; [3]Physics, The Pennsylvania State University, University Park, Pennsylvania.

High frequency mechanical resonators operating in the frequency range of 1GHz and higher are of great interest in RF applications. However, even using the torsional mode of operation, micron sized resonators are typically limited to a maximum frequency of $\sim$1 GHz. One way to achieve further improvements in resonator characteristics is to use higher stiffness materials. Carbon nanotubes (CNTs) have been measured to have very high axial modulus of elasticity $\sim$1 TPa. Incorporation of the high modulus CNTs into MEMS thin films is expected to improve the elastic properties of deposited thin films. We incorporated CNTs in MEMS structures in two different ways and independently observed an increase in the stiffness of the micromechanical structure. In this paper we report the first observation of the improvement of the stiffness of MEMS structures by addition of CNTs. A detailed analysis of the observed improvement in the mechanical properties of thin films and the practical implications of these findings for MEMS devices will be explored. In the first technique, CNT bundles were incorporated into PECVD Si_3N_4 thin films. This was done by a sequential deposition of Si_3N_4 and CNT layers onto a plain Si substrate. CNTs were deposited using an airbrush spray technique. To test the mechanical properties, the Si_3N_4-CNT composite layer was patterned by reactive ion etching followed by a release in XeF2 to create freestanding bridge structures. A control sample was created by the same layered deposition of Si_3N_4 but without the CNTs. The bridges were tested with an AFM system to obtain Force-Displacement (F-D) curves. Slope of the curve gave the spring constant of the AFM tip and bridge in series. 50 F-D curves were taken around the center of each bridge and the average spring constant was calculated. An average increase in combined spring constant of $\sim$20 nN/μm was observed compared to the control bridges. In the second technique, bridges fabricated using dissolved wafer process were spray coated with single walled CNTs (SWNTs). Since the SWNTs are suspended in NMP solvent, the spray coating was done locally on each bridge using a piezoelectric printhead. Resonance frequency measurements were done in vacuum on the bridges after successive SWNT depositions. An increase in the resonance frequency was observed which can be attributed to an increase in the stiffness due to the surface incorporation of SWNTs. A distinct logarithmic gas desorption behavior of the CNTs was inferred from the change in resonance frequency with time. Such logarithmic desorption behavior was not observed for uncoated bridges. A maximum change of $\sim$37.9% (effective modulus of 237 GPa for B$-$doped Si) was inferred from resonance frequency changes.

SESSION O2: Characterizing Thin Films by Nanoindentation

Chair: Andrew Minor
Tuesday Morning, March 29, 2005
Room 2022 (Moscone West)

10:30 AM *O2.1

Nanoindentation and Raman Microspectroscopy Study of Semiconductors and Ceramics. Yury Gogotsi, Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

In many applications of materials, their surface experiences a contact with another material and takes the external load before the bulk of the material is influenced. Often, only the outermost surface layer or coating having the thickness from nanometers to micrometers is affected by the surface contact. This kind of loading has a very significant nonhydrostatic component of stress that may lead to dramatic changes in the material structure, such as amorphization and phase transformation. During contact interactions, when a hard indenter (e.g., diamond) touches the surface of another hard material (ceramic or semiconductor), very high pressures can be achieved because the contact area in the beginning of the penetration of the sharp indenter into material is small. These pressures can exceed the phase transformation pressure for many materials. Simultaneously, processes of plastic deformation, fracture and interactions with the environment and counterbody can occur. The latter have been described in numerous publications, but the processes of phase transformations at the sharp contact were investigated only during past decade and the data obtained have only recently been summarized [1]. Understanding and appreciation of phase transformations induced by contact loading can help to understand the mechanisms of wear, friction and erosion. A combination of depth-sensing indentation and Raman spectroscopy is the most powerful tool for studying phase transformations, damage and residual stresses induced by contact loading. The paper will describe the use of nanoindentation and Raman microspectroscopy to study phase transformations and amorphization that occur in ceramics and semiconductors. Reference: 1. High Pressure Surface Science and Engineering, Ed. Y. Gogotsi & V. Domnich, Institute of Physics Publishing, Bristol, UK, 2003

11:00 AM O2.2

Application of Depth-Sensing Macro/Nano Indentation and Micro-FTIR Spectroscopy for Understanding the Weathering Performance of a Coated Engineering Thermoplastic Blend. Samik Gupta[1], Jan Lohmeijer[2], Savio Sebastian[1], Nisha Preschilla[1] and Amit Biswas[1]; [1]Polymers and Synthetic Materials, GE India Technology Centre, Bangalore, Karnataka, India; [2]Advanced Materials, GE, BOZ, Netherlands.

Coatings are applied on engineering thermoplastics(ETP's) for aesthetics and for protecting the bulk of the material from harsh weathering environments. The degradation of material performance upon weathering typically starts from the surface and then proceeds inwards to the bulk of the material. We have used a novel combination of depth-sensing macro and nano-indentation and micro-FTIR techniques to investigate the effect of weathering in a coated ETP.Nano-indentation was used to study the mechanical properties of the coating upon weathering while micro-indentation provided insights into the mechanical performance of the substrate in combination with the coating.Weathering of organic coatings and substrates is accompanied by chemical changes, which can be monitered very effectively by depth-dependent micro-FTIR spectroscopy. This unique combination of depth-sensing indentation and micro FTIR spectroscopy led to an understanding of not only the individual contributions of the coating and the substrate, but also the interaction of the two at the interface as a function of weathering exposure time.

11:15 AM O2.3

Mechanical Characterization of Multilayer Thin Film Stacks Containing Porous Silica Using Nanoindentaion and the Finite Element Method. Ke Li[1], Raghu Mudhivarthi[2,3], Roja Gottimukkala[2,3], Sunil Saigal[1] and Ashok Kumar[2,3]; [1]Department of Civil & Environmental Engineering, University of South Florida, Tampa, Florida; [2]Department of Mechanical Engineering, University of South Florida, Tampa, Florida; [3]Nanomaterials and Nanomaunfacturing Research Center, University of South Florida, Tampa, Florida.

Novel metal/dielectric material combinations are becoming increasingly important for reducing the resistance-capacitance (RC) interconnection delay within integrated circuits (ICs) as the device dimensions shrink to the sub-micron scale. Efficient electric connections require the use of metals with low resistivity and dielectric materials with a low dielectric constant (K). Copper (Cu) is believed to be one of the best choices for metal interconnects, and silica (SiO2) has been commonly utilized as an interlayer dielectric material (with $K = \sim 3.9$) in the industry. To improve the performance of high speed ICs, dielectric materials with much lower values of K are needed. One plausible way of achieving this goal is to introduce air voids (porosity) into SiO2. However, the increase of porosity undermines the mechanical reliability of the dielectric layer and hence the entire device. The objective of the current work is to examine the effects of porosity on mechanical properties of a multilayer thin film (Cu and SiO2)-substrate (Si) system using nanoindentaion and the finite element (FE) method. An FE model is first developed to simulate the nanoindentation of bulk Cu and SiO2 samples. Once the model is validated by comparing the predicted load-displacement curves with those obtained from experimental tests, a parametric study is performed by extending the FE model to the Cu/ SiO2/Si system with the porosity of SiO2 and the thicknesses of the two thin film layers as the controlling parameters. Mechanical properties such as loading-unloading behavior with respect to the indentation depth, elastic modulus, and hardness are then obtained from the FE simulations.

11:30 AM O2.4

Model for the Indentation Size Effect Taking into Account Nanoindenter Tip Bluntness. Ju-Young Kim[1], David T. Read[2] and Dongil Kwon[1]; [1]School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; [2]Materials Reliability Division, National Institute of Standards and Technology, Boulder, Colorado.

Nanoindentation is used extensively to measure the hardness of materials. Hardness values are commonly observed to depend on indentation depth, especially in the nanometer range, so that the hardness value at a given depth is not the same as that at a different depth. It is thus essential to characterize the variation in hardness with indentation depth. An increase in hardness with decreasing indentation depth, the well-known indentation size effect (ISE), has been observed in numerous nanoindentation experiments on various materials [1-2]. This increase is believed to be associated with the geometrically necessary dislocations (GNDs) induced by imposed strain gradients [3-4]. Nix and Gao clarified the ISE for crystalline materials by considering the GND density around a conical indenter [5]. However, the Nix-Gao model uses an ideally sharp indenter tip geometry, while some degree of bluntness is inevitable at the tip of a sharp indenter such as the Berkovich indenter generally used in nanoindentation experiments. Therefore, the Nix-Gao model does not completely describe the variation in hardness with indentation depth for depths less than about 100 nm [5-7]. This issue is critical in the ISE characterization of micromaterials, where the indentation depth is limited. This study presents an improved ISE model that considers both the effect of tip bluntness on the GND distribution needed to accommodate a blunt-tip conical indenter and the change in the ratio of plastic to total contact depth with contact depth. The ISE depends on indenter tip shape since GNDs, the main cause of ISE, are required to accommodate the surface inhomogeneous plastic deformation caused by indentation. The actual indenter geometry is not self-similar because of tip bluntness, so the ratio of plastic to total contact depth at shallow contact depths changes with contact depth. We related these two tip-bluntness effects to parameters that are easily observed in the nanoindentation test, allowing convenient application of the present model. Nanoindentation experiments using a Berkovich indenter were conducted on single-crystal, polycrystalline, and amorphous materials at various contact depths. The results show excellent agreement of the present model with nanoindentation data, including shallow contact depths. We also showed that the present model leads to a reasonable characteristic relation for the ISE. REFERENCES [1] Q. Ma and D.R. Clarke, J Mater Res 10, p. 853 (1995). [2] K.W. McElhaney, J.J. Vlassak, and W.D. Nix, J Mater Res 13, p. 1300 (1998). [3] N.A. Fleck and J.W. Hutchinson, J Mech Phys Sol 49, p. 2245 (2001). [4] J.G. Swadener, E.P. George, and G.M. Pharr, J Mech Phys Sol 50, p. 681 (2002). [5] W.D. Nix and H. Gao, J Mech Phys Sol 46, p. 411 (1998). [6] Y. Wei, X. Wang, and M. Zhao, J Mater Res 19, p. 208 (2004). [7] T.-Y. Zhang, W.-H. Xu, and M.-H. Zhao, Acta Mater 52, p. 57 (2004).

11:45 AM O2.5

Characterizing Viscoelastic Behavior Using Nanoindentation. Mark R. VanLandingham[1], Thomas F. Juliano[1] and Peter L. Drzal[2]; [1]Materials Division, U. S. Army Research Laboratory, Aberdeen Proving Ground, Maryland; [2]Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

Instrumented indentation, sometimes referred to as nanoindentation, is increasingly being used to probe the mechanical response of polymeric materials. In contrast to traditional engineering materials (i.e., metals and ceramics) to which indentation techniques have most often been applied, the characterization of polymers by a single modulus or hardness values is often of limited value because of their viscoelastic nature. Additionally, polymers often behave in a nonlinear fashion at relatively small levels of strain, and their responses to tension, compression, or shear can be quite different. Thus, a number of challenges exist to applying instrumented indentation methods to polymeric materials. In this presentation, the use of nanoindentation to characterize polymeric materials is discussed, including quasi-static (creep and stress relaxation) and dynamic methods of both glassy and rubbery polymers at room temperature using a variety of tip geometries. Data from traditional solid rheometry measurements are compared to the indentation data. Current limitations and opportunities for improvement will be discussed.

SESSION O3/BB2: Joint Session: Mechanical Behavior of Nanostructured Films

Chairs: Peter Anderson and Erica Lilleodden
Tuesday Afternoon, March 29, 2005
Room 2016 (Moscone West)

1:30 PM *O3.1/BB2.1

Plastic Strength Maps for Metallic Multilayer Thin Films. Peter M. Anderson, Dept of Materials Science and Engineeering, Ohio State University, Columbus, Ohio.

From an engineering perspective, new classes of materials benefit from a knowledgebase from which properties can be viewed as a function of structure. For metallic multilayer thin films, such structural parameters include the multilayer period, volume fraction of phases, interfacial properties between phases, and individual properties of phases such as elastic moduli and stress-free lattice parameter. This presentation discusses the development of plastic strength maps for metallic A/B multilayer thin films. The maps are based on the premise that bulk plastic yield occurs when dislocation loops are able to percolate throughout the multilayer thin film. A simple assumption for percolation is that the film is stressed and deformed in tension sufficiently to eliminate compression in any of the alternating layers. The resulting maps predict contours of constant plastic strength for a given A/B system, as a function of bilayer period and volume fraction of phases. Two implications are that volume fraction may be a relatively potent parameter to increase plastic strength, particularly in the "strength plateau" region at small bilayer period. Second, multilayer thin films are predicted to have a large asymmetry in bulk yield strength in tension versus compression, similar to bulk layered composite materials.

2:00 PM O3.2/BB2.2

Atomic-Scale Analysis of Strain Relaxation Mechanisms in Ultra-Thin Metallic Films. M. Rauf Gungor and Dimitrios Maroudas; Department of Chemical Engineering, University of Massachusetts, Amherst, Amherst, Massachusetts.

Atomic-scale modeling based on molecular-dynamics (MD) simulation provides a powerful means for analyzing atomistic mechanisms of strain relaxation in metallic thin films and enables the development of constitutive equations for continuum modeling of metallic thin-film mechanical behavior. The results of such modeling are particularly important for model-based prediction of materials reliability in today's nanoscale electromechanical devices. In this presentation, we report a comprehensive computational analysis of the atomistic mechanisms of strain relaxation and failure under a wide range of applied biaxial tensile strain in free-standing Cu thin films with the film plane oriented normal to the [111] crystallographic direction. The analysis is based on isothermal-isostrain MD simulations within an embedded-atom-method (EAM) parameterization for Cu and using slab supercells that contain millions of atoms with and without cylindrical voids normal to the film plane and extending throughout the film thickness. Our analysis has revealed various regimes in the film's mechanical response as the applied strain level increases. After an elastic response at low strain (< 2%), plastic deformation occurs accompanied by dislocation emission from the void and film surfaces, void surface morphological transitions, dislocation jogging, vacancy generation by jogged dislocations, vacancy pipe diffusion along dislocation cores, dislocation-vacancy and dislocation-dislocation interactions, as well as formation and propagation of threading dislocation loops. At the lower strain range following the elastic-to-plastic deformation transition (< 6%), void growth is the major strain relaxation mechanism mediated by emission of perfect screw dislocation dipoles from the void surface and subsequent dislocation propagation; as a result, a plastic zone forms around the void. At higher levels of applied strain (> 6%), a subsequent transition to a new plastic deformation regime gives rise to a practically uniform distribution of dislocations in the metallic thin film. Under such conditions, dislocations are emitted from the free surfaces of the thin film and inhibit void growth as the dislocations emitted from the void surface are pinned by their interaction with the simultaneously generated dislocations from the film's surface. By comparing MD simulation results in identical thin films with and without voids, it is also demonstrated that strain relaxation at high levels of strain is not affected by an existing void in the metallic film.

2:15 PM O3.3/BB2.3

Deformation Mechanisms during Nanoindentation of Ultrafine and Nanocrystalline Metals. Miao Jin[1], Andrew M. Minor[2], Daibin Ge[2], Eric A. Stach[3] and J. W. Morris, Jr.[1]; [1]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [3]School of Materials Engineering, Purdue University, West Lafayette, Indiana.

The plastic deformation mechanisms of materials with grain sizes in the nanoscale regime (1-500nm) are still largely debated. Recent experimental results and computational simulations show that grain boundary sliding and/or grain rotation can become dominant deformation modes when grain sizes shrink to below some critical size (on the order of 10 nm). In this work, we combine conventional ex situ nanoindentation with in situ nanoindentation in a TEM in order to gain insight into the relevant deformation mechanisms for ultrafine-grained and nanocrystalline Al films. We will present real-time videos that show that stress-induced grain growth- resulting from grain boundary migration, grain rotation and grain coalescence- is a common occurrence in these materials as the indentation proceeds. Our results suggest that grain growth and coalescence in these inherently metastable microstructures appear to be important modes of response in the deformation of ultrafine-and nanograined materials.

2:30 PM O3.4/BB2.4

In-Situ Peak Profile Analysis of Submicron Aluminum Thin Films in Tension. D. S. Gianola[1], S. Brandstetter[2], K. J. Hemker[1], A. Cervellino[2] and H. Van Swygenhoven[2]; [1]Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland; [2]Paul Scherrer Institute, Villigen, CH-5232, Switzerland.

Mechanical properties of metals are altered when scaling down sample dimensions to the micron scale and/or structural length scales (for instance grain size) to the nanometer scale. In order to study the deformation behavior while concurrently sampling information on the structural changes in a material, a novel in-situ tensile testing technique that uses synchrotron X-rays to track the Bragg peaks during the evolution of straining is utilized. This experiment has been developed at the Swiss Light Source and uses a microstrip detector that covers an angular range of 60°, allowing for the measurement of several diffraction peaks at once during deformation. The specimens are fabricated using MEMS-inspired processes on Si wafers such that the freestanding films span across a rigid Si frame, which alleviates challenges associated with handling of fragile samples. Al is deposited by pulsed DC-magnetron sputtering onto the Si substrate to yield high-purity specimens. Free standing thin films of thicknesses of 200 and 400 nm with mean grain sizes of approximately 40 and 90 nm, respectively, are deformed during tensile load-unload and stress relaxation cycles. The mechanical behavior is represented by means of tensile measurements of yield stress, UTS, total strain and activation volume. The peak broadening in terms of applied stress and a careful TEM characterization of the thin films before and after deformation reveal the underlying deformation mechanisms in submicron thin films. The peak shift in terms of the applied stress allows the determination of Young's modulus. The results will be discussed in terms of both thickness and grain size.

2:45 PM O3.5/BB2.5

Behavior of Individual Grains in Nanocrystalline Ni during Deformation. Zhiwei Shan[1], Eric Stach[2], James Knapp[3], David Follstaedt[3], Jorg Wiezorek[4] and Scott Mao[1]; [1]Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California; [3]The Physical, Chemical and Biomolecular Sciences Center, Sandia National Laboratories, Albuquerque, New Mexico; [4]Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

The dynamic behavior of individual grains in nanocrystalline Ni during deformation has been studied by in situ tensile straining, bright-field transmission electron microscope and micro beam electron diffraction observations under low local strain rate. It was found that grain boundary mediated processes contributed prominently to plastic deformation, as predicted by theoretical consideration as well as molecular dynamics simulations for ductile metals with a grain size below a critical value. Moreover, it was found that interiors of nano-sized grains experience severe lattice distortions during the deformation. This observation apparently challenges the generally invoked assumption that interiors of nano-sized grains behave as a rigid body during deformation. Based on our experimental TEM observations as well as other recently reported experiments results, a unifying picture for the unusual deformation mechanism for nanocrystalline face-centered-cubic metals is proposed. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

3:30 PM O3.6/BB2.6

Grain Agglomeration in Nanocrystalline Ni. Zhiwei Shan[1], David Follstaedt[2], James Knapp[2], Eric Stach[3], Jorg Wiezorek[4] and Scott Mao[1]; [1]Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; [2]Physical and Chemical Science Center, Sandia National Laboratories, Albuquerque, New Mexico; [3]School of Materials Engineering, Purdue University, West Lafayette, Indiana; [4]Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Tensile to fracture of full dense nanocrystalline metals often exhibit a dimple morphology at the fracture surface with characteristic dimple sizes much larger than that of the average grain size. By exploring in situ tensile transmission electron microscopy tests on high quality, free stranding nanocrystalline Ni films with an average grain size of about 10nm, it was found grain agglomerates formed very frequently and rapidly in many locations apparently independently of one another through collective rearrangements of groups of neighboring grains under influence of the applied stress. Guided by the changes documented in the Ni films during the in situ TEM tests, we propose that the dimple structures observed on fracture surfaces could result from the collective motion of those newly formed agglomerates and those pre-existed "nano domains". Implications of the dynamic TEM observations as well as the proposed interpretation on the strength and ductility of nanocrystalline materials are discussed. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC-94AL85000.

3:45 PM O3.7/BB2.7

Characterization and Mechanical Behavior of Cu/Cu Nano-Laminates. Andrea Maria Hodge[1,2], Y. Morris Wang[1,2] and Troy W. Barbee Jr.[1]; [1]Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Nanoscale Synthesis and Characterization Laboratory, Lawrence Livermore National Laboratory, Livermore, California.

The development of atomic level deposition of layers has allowed the fabrication of free-standing nano-laminates, also known as multilayers. These multilayers incorporate the structural advantages of both composites and nano-crystals, which makes them candidates for a wide range of applications. In this talk, we will concentrate on high purity (99.999%), fully dense, free-standing Cu/Cu nano-laminates, produced by DC magnetron sputtering, and composed of nanometer-sized layers of Cu with thickness ranging from 1.2 nm to 43.6 nm. The macroscopic thickness of the nano-laminate samples was $\sim$25 microns, which, depending on the layer thickness, contained from 520 to 18,000 layers. The nano-laminates were characterized by depth sensing nanoindentation and Vickers microhardness on their top and bottom surfaces (normal to the layering) and parallel to the layers. These tests showed hardness values on the order of 2.5 to 3.0 GPa, a substantial increase in strength over conventional polycrystalline Cu. Our results present a trend towards a Hall-Petch plateau for grain sizes below 10nm. This result differs from previous work on nanocrystalline materials synthesized using other technologies with grain sizes less than 10 nm, which showed a trend towards a reverse Hall-Petch behavior. Extensive plan view and cross-section transmission electron microscopy (TEM) demonstrates the nanocrystallinity of the Cu/Cu multilayers as well as extensive twinning. This allows us to compare the effects on grain size and twinning by individual layer thickness and to relate this to the hardness and yield strength of these Cu/Cu nano-laminates. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract of No.W-7405-Eng-48.

4:00 PM O3.8/BB2.8

Mechanical Properties and Deformation under Nanoindents in Metal/Nitride Nanoscale Multilayers. Gregory Abadias[1], Yau-Yau Tse[1], Anny Michel[1], Christophe Tromas[1] and Sergey N. Dub[2]; [1]Laboratoire de Metallurgie Physique, UMR 6630, Universite de Poitiers, Futuroscope-Chasseneuil, France; [2]Institute of Superhard Materials, Kiev, Ukraine.

Mechanical behavior and stability of thin film structures consisting of alternating nanolayers have been the subject of great research activity over the past decade due to the technological impact of such nanoscale systems, but also to understand the plastic mechanisms operating at small-scales. Enhancement of hardness and tensile strength as compared to the rule of mixture values for their bulk phase counterparts have been reported in a large variety of systems. These include the case of isostructural, miscible metal/metal or nitride/nitride multilayers, but also non-isostructural and immiscible systems, such as Mo/NbN or W/NbN. However, the exact deformation mechanisms operating under nanoindentation tests (dislocation pileups, dislocation motion within individual layers, grain boundary sliding...) have not been clearly established. In particular, the case of nanolayers combining elastically soft metal (Cu, Ag, ...) and hard nitride (TiN) layers remains to be investigated. The present study reports new data on the structure and mechanical properties of such nanocomposite multilayers. Three nanolayered systems, namely TiN/Cu, TiN/Ag and TiN/W, corresponding to different crystal structure and lattice mismatch combinations, have been considered. They were deposited at room temperature using a dual-target ion beam sputtering in Ar-N2 mixtures, on Si wafers and MgO(001) substrates. The bilayer period —*lambdaup*— was varied between

2.5 and 50 nm and the total film thickness was equal to ~0.2 μm. Low-angle and high-angle X-ray diffraction experiments as well as TEM observations were used to characterize the microstructure and crystalline orientation, structure of interfaces and type of growth defects. Mechanical properties were studied by nanoindentation tests using a Berkovich tip and coupled with Atomic Force Microscopy surface observations around the indents. Also, a combined FIB-TEM technique was implemented to image the deformed nanolaminates beneath the indentor. In all systems, low-angle XRD patterns exhibited a large number of superlattice reflections, attesting the good reproducibility of the stacking along the growth direction. For the TiN/Cu system, a cube on cube epitaxial growth with semi-coherent interfaces was observed. Detailed analysis of the hardness values vs. contact depth ratio gave access to the intrinsic film hardness. No enhancement of hardness was found for the case of Cu/TiN and Ag/TiN over the rule of mixtures values, in contradiction with predictions of existing theoretical models. A visco-elastic behavior is rather suggested. The different mechanical behavior are discussed in terms of film microstructure, presence of residual stress and influence of interfacial structure.

4:15 PM O3.9/BB2.9

Thermal Plasma Chemical Vapor Deposition of Superhard Nanocrystalline Silicon Carbide Films. Steven L. Girshick[1], Feng Liao[1], William M. Mook[2], Michael R. Zachariah[3] and William W. Gerberich[2]; [1]Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota; [2]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; [3]Mechanical Engineering, University of Maryland, Minneapolis, Maryland.

Superhard nanocrystalline silicon carbide films were deposited using thermal plasma chemical vapor deposition. Silicon tetrachloride vapor and methane were injected into an argon-hydrogen plasma generated by radio-frequency (RF) inductive coupling. The flow rates were as follows: argon, 42.5-60 slm; hydrogen, 0.5-2.5 slm; silicon tetrachloride, 68-140 sccm; and methane, 80-140 sccm. The plasma issued from the RF torch into a chamber maintained at a pressure of 33.3 kPa. Molybdenum substrates were mounted on-axis and normal to the flow. Substrate temperatures ranged from 750-1250 C. Deposition rates were extremely high, ranging up to approximately 900 microns/h, as measured by micrometer, for silicon tetrachloride flow rates of 140 sccm. Scanning electron microscopy images of film cross sections showed columnar growth, while the film top surfaces were characterized by hemispherical balls that were composed of nanocrystalline grains. The grain size as determined from X-ray diffraction (XRD) using the Warren-Averbach method ranged from 4-27 nm. XRD showed the films to consist of the cubic phase, 3C-SiC, with a pronounced (111) orientation. For substrate temperatures above 1100 C the XRD peak associated with (200) was additionally observed. RBS measurements indicated that the films were in most cases close to stoichiometric SiC. Analysis of the XRD spectra suggested that the films consisted of SiC nanocrystallites in an amorphous SiC matrix, with the degree of crystallinity ranging from 40-100 percent. Neither XRD nor Raman spectroscopy indicated the presence of a diamond phase. Nanoindentation was used to measure the film hardness, modulus and fracture toughness. Two different nanoindenters were used, a Hysitron TriboIndenter and an MTS Nano Indenter XP. Measurements were made both of film cross sections and of film top surfaces, in both cases first polishing the surfaces. The hardest film measured had average hardness values for indentations into the cross section of 51 GPa and 56 GPa, as measured by the Hysitron and the MTS instruments, respectively, and 48 GPa for top-down indentation (MTS), with modulus values around or slightly above 500 GPa. Several other films tested also had hardness values in the superhard range, above 40 GPa. In general we found a strong correlation between the hardness and the substrate temperature, with the superhard films being deposited at temperatures above 1100 C. The grain size for these films lay in the range 6-20 nm, and the fractional crystallinity was in most cases in the range 80-85%. Fracture toughness was determined for several films using Vickers indentation of the polished top surface. Measured values ranged up to 4.8-4.9 MPa-m1/2. These films are much harder than standard SiC (about 28 GPa). A detailed investigation of the cause of these exceptional mechanical properties is currently in progress.

4:30 PM O3.10/BB2.10

Thermal Plasma Chemical Vapor Deposition of Superhard Nanostructured Si-C-N Coatings. Nicole J. Wagner[1], Megan Cordill[2], Lenka Zajickova[1], Joachim V. R. Heberlein[1] and William W. Gerberich[2]; [1]Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota; [2]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota.

Materials that protect against erosion, wear, and other harmful degradation are of great interest for various industries to coat, for example, automotive engine parts and machining tools. Superhard nanostructured composite coatings offer enhanced mechanical properties that would reduce and possibly eliminate the necessity of costly and hazardous coolants for such applications. While many methods to produce such materials exist, the thermal plasma chemical vapor deposition (TPCVD) process allows the possibility of using versatile multiphase reactants and producing a controllable film structure at high growth rates. In this study, a triple torch plasma reactor was used to synthesize nanostructured Si-C-N composite films via the TPCVD process. The argon-nitrogen plasma provided atomic nitrogen to the multiphase reactants. Carbon- and silicon-based reactants were injected through a central injection probe and ring configuration at flow rates ranging from 0.01-0.20slm. The deposition pressures ranged from 100-200Torr and the substrate temperatures from 900-1400°C. Comparisons are made between variations of the carbon-based reactants (methane and acetylene), silicon-based reactants (silicon tetrachloride and hexamethyldisilazane), and the substrate material (silicon and molybdenum) and pretreatment (roughening and carbonization). The advantages for using each reactant in the gas mixture were investigated. While the depositions made on molybdenum substrates appeared more uniform than those on silicon, the adhesion of the films was reduced. Micro X-ray diffraction was used to verify the presence of silicon nitride, silicon carbide, carbon nitride and carbon in the films. Both α-Si_3N_4 and β-Si_3N_4 diffraction peaks were seen to be dominant for most of the depositions. The bonding of amorphous phases was investigated using Fourier transform infrared spectroscopy. Although many possibilities of bonding existed for this Si-C-N-H system, infrared bands indicated the presence of N-H, Si-H and C≡N or C≡C in various films. Indentation tests were conducted on the polished film cross-sections and surfaces to determine the hardness and elastic modulus of the depositions. Large variations in mechanical properties were observed for minor changes in film composition. In addition, the substrate temperature has a significant effect on mechanical properties. Correlations between indentation results and scanning electron and optical microscope images showed that the mechanical properties greatly depend on the film morphology; the denser, smoother, and more crystalline films tended to display enhanced mechanical properties. Acknowledgements: Funding provided by the Department of Energy Grant No. DE-FG02-85ER13433 Ao15, the National Science Foundation Integrated Graduate Education and Research Traineeship Grant No. DGE-0114372, and the National Science Foundation North Atlantic Treaty Organization Postdoctoral Fellowship Grant No. DGE-0312210.

4:45 PM O3.11/BB2.11

Depth Profiling of Mechanical Properties on the Nanoscale of Single Layer and Stepwise Graded DLC Films by Nanoindentation and AFM. Carlos Ziebert, Sven Ulrich, Michael Stueber and Helmut Holleck; Institut fuer Materialforschung I, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

The stepwise graded layer concept adjusts a graded constitution of the growing film by a stepwise increase of the ion energy, i.e. the bias voltage, during magnetron sputtering [1]. In order to optimise this concept, which has been developed to manage the high internal stresses of thick diamond-like carbon films (DLC), a depth profiling of the mechanical properties particularly in the interface regions between the layers sputtered with different bias voltage is extremely important. The deposition started with a bias voltage of 0 V to initiate a high adhesion of the growing film. Then the bias voltage was increased stepwise to -150 V and finally to -300 V to produce a hard film surface. To investigate the influence of the thicknesses of the three graded layers on the thickness of the interface regions different layer deposition time characteristics and thus thickness ratios of the three graded layers were adjusted. When the load variation nanoindentation method was used, where the indenter probes deeper and deeper regions of the sample by increasing the applied load, the depth profile becomes smeared because of the combined mechanical behaviour of the film and the hard metal substrate. However, by using the small angle cross-section nanoindentation method (SACS) it was possible to record depth profiles of the hardness, the elastic modulus and the yield stress with nanometer resolution and to investigate the evolution of these mechanical properties with increasing annealing temperature. In this method the area on the differently graded layers is drastically enlarged by preparing a cross-section under a very small angle of about 0.02 to 0.15 and° the distance travelled by the nanoindenter is translated into depth information using a simple geometric formula. It was revealed that the thickness of the interface regions is mainly determined by the thickness ratio of the graded layers. In addition changes in fracture and crack propagation behaviour of single and stepwise graded DLC films have been investigated by nano- and microindentation using a Berkovich indenter and ex-situ AFM-imaging with respect to ion bombardment during sputter deposition and the thickness of the interface regions between the graded layers. Future research will be focused on optimising the interfaces between the graded layers to further enhance the temperature stability, the maximum achievable thickness and the fracture toughness. Therefore additional theoretical and experimental studies will be needed to improve the understanding of the behaviour of mechanical layer properties across interfaces. [1] H. Holleck and M. Stueber, Method of manufacturing a composite material structure, US Patent No. 6, 110, 329 (2000); EU Patent No. EP 0912774B1 (2002).

SESSION O4: Poster Session: Mechanical Properties of Thin Films - Testing and Analysis

Chairs: Thomas Buchheit, Andrew Minor, Ralph
Spolenak and Kazuki Takashima
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)

O4.1

Experiments on the Elastic Size Dependence of LPCVD Silicon Nitride.

Yuxing Ren and David C. C. Lam; Mechanical Engineering, HKUST, Hong Kong, China.

In classical elasticity, geometric dependence of the rigidities can be normalized and the normalized rigidities are size independent. Recent experimental observations showed significant elastic size effect in normalized bending rigidity in micron scale epoxy beams. Size effect in elastic behaviors can be described by surface stress theories and strain gradient elasticity theories. Surface effect on elastic properties is significant in nanometer scale, but recognized to be negligible in micron scale. The observed size effect in micron sized epoxy beams was found to agree with strain gradient elastic models. Besides epoxy films, effort is underway to characterize strain gradient behaviors in other material systems. Silicon nitride thin film is a widely used film in MEMS. Comprehensive understanding of the elastic deformation behaviors of silicon nitride thin films is essential for design and analysis of MEMS structures. In this investigation, submicron thick LPCVD silicon nitride thin films were fabricated. XPS and XRD analyses were conducted to determine elemental and micro-structural consistency of the as-fabricated thin films. XPS analyses showed element compositions were similar in films with different thicknesses. However, XRD analyses revealed that films had different crystalline phase fractions. Cantilever beams were fabricated from the films and elastic bending tests on the beams were conducted using nanoindenter to investigate the elastic bending behaviors of the films as a function of thickness. Analyses showed that beams with different thickness had fluctuating normalized bending rigidities. The fluctuations of normalized bending rigidities maybe related to varying crystalline phase fractions in the thin films. The beams were annealed and bending tests were conducted to investigate possible correlation between normalized bending rigidity fluctuations and crystalline phase fractions. Bending tests results showed similar level of fluctuations in normalized bending rigidities before and after annealing while XRD results of the annealed films showed increase in crystalline phase fractions for all thicknesses. This suggested crystalline phase fraction cannot be correlated with the fluctuations in normalized bending rigidities of the beams. Error analyses of experiment setup, geometries of the beams and data analysis were conducted. The fluctuations in normalized bending rigidity in different thickness were within the error range. While LPCVD silicon nitride may have size dependence in the nanometer scale, size dependence of normalized bending rigidity of LPCVD silicon nitride appears to be insignificant in submicron scale. Design of silicon nitride MEMS structures can be modeled with conventional elasticity without considerations for size effects.

O4.2

Correction of Film Thickness Measurement using Numerical Simulation and Semi-Empirical Models of Indentation.

Hamed Lakrout[1] and Greg F. Meyers[2]; [1]Materials Research, The Dow Chemical Company, Midland, Michigan; [2]Analytical Sciences, The Dow Chemical Company, Midland, Michigan.

Film thickness is a critical input to evaluate coating properties such as dielectric constant for low-k materials. Mechanical film thickness is often employed for this measurement by first scratching the film and then profiling its thickness. A materials science-based method for understanding and prediction of the precision and accuracy of mechanical thickness measurement is needed. In the case of thin film dielectrics, the measurement involves contact mechanics between a tip of known shape and a film surface under a prescribed load. Prior studies have shown that there is a load dependent thickness reduction when measuring the thickness of an elasto-plastic coating on silicon wafer substrates. A Hertz linear elastic analysis can explain general trends. In this work, we have achieved a better understanding using numerical simulations and semi-empirical models from the literature. A series of indentation experiments has been performed on a SiLK* Semiconductor Dielectric film covering a large series of thickness with a wide range of loads using a KLA-Tencor P-15 stylus profilometer. An indentation model has been designed in ABAQUS$^{(tm)}$ based on the tensile materials properties of the coating. Experimental data and numerical simulations are compared to analytical semi-empirical models in which the thickness effect is interpreted as a variable effective modulus. We find that there is a good match between the predictive model and the experiments at low loads with some discrepancies at higher loads. Numerical and analytical models currently available in the literature do not accurately reproduce elasto-plastic materials mechanical behavior. *Trademark of The Dow Chemical Company

O4.3

Evolution of Wrinkles in a Compressed Elastic Film on a Viscoelastic Layer.

Rui Huang and Se Hyuk Im; Department of Aerospace Engineering and Engineering Mechanics, University of Texas, Austin, Texas.

This paper develops a theoretical model for wrinkling of an elastic film on a viscoelastic layer. The film is elastic and subjected to a compressive residual strain. The viscoelastic layer is sandwiched between the film and a rigid substrate. The nonlinear von Karman plate theory is employed to model the film, and a thin-layer approximation is adopted for the viscoelastic layer. The stability of the system and the kinetics of wrinkle evolution are studied first by a linear perturbation analysis and then by numerical simulations, both for plane strain deformation only. Three stages of evolution are identified: initial growth of the fastest growing mode, intermediate growth with mode transition, and finally an equilibrium state. The results qualitatively agree with experimental observations with a metal film on a polymer layer.

O4.4

Effect of Residual Stress on Nanoindentation Behavior of Materials.

Zhi-Hui Xu and Xiaodong Li; Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina.

The existence of residual stress in materials has a large influence on the nanoindentation behavior of materials. Residual stress changes the piling-up or sinking-in behavior of materials, which is normally dependent on the mechanical properties of materials. In this paper, two-dimensional finite element simulation has been carried out to investigate the effect of the existing residual stress on the indentation behavior of elastic-plastic strain-hardening materials with different elastic modulus/yield strength ratios and strain-hardening exponents. Biaxial stresses have been applied to the finite element model. The variation of the ratio of the elastic recovery to the maximum penetration depth with the applied stresses has been studied. It is found that the elastic recovery to the maximum penetration depth ratio, which is an experimental parameter that can be directly determined from the unloading curve of indentation, is very sensitive to the changes of the contact area of indentation caused by the residual stresses. The elastic recovery to the maximum penetration depth, which has a linear relationship with the residual stresses, increases with the increasing compressive residual stress and decreases with the increasing tensile residual stress. This relationship may provide a useful way for the determination of residual stress by nanoindentation testing.

O4.5

Thermomechanical Behavior and Properties of Passivated PVD and ECD Cu Thin Films.

M. Gregoire[1], S. Kordic[2], P. Gergaud[3], O. Thomas[3] and M. Ignat[4]; [1]STMicroelectronics, Crolles2 Alliance, Crolles, France; [2]Philips Semiconductors, Crolles 2 Alliance, Crolles, France; [3]University of Aix-Marseille III, TECSEN-UMR CNRS, Marseille, France; [4]Institut National Polytechnique of Grenoble, LTPCM-UMR CNRS, Saint Martin d'Heres, France.

Copper thin films fabricated using Physical Vapor Deposition (PVD) and Electrochemical Deposition (ECD) are widely used in modern microelectronic industry. It is well known that high internal stresses in such films can lead to important failure mechanisms such as spontaneous cracking and interfacial delamination [1]. In addition, film properties such as texture and grain size are significant to electromigration and stress voiding behavior [2]. Therefore, prediction and improvement of thin film reliability require detailed knowledge of film stresses and film mechanical behavior. However, up until now the vast majority of studies deal with e-beam sputtered Cu films, which are hardly used nowadays in modern IC manufacturing, while the thickness of these films does usually not exceed 1 μm [3, 4]. In this paper, thermomechanical properties and behavior of self-annealed blanket Cu films are discussed. These films are deposited using standard IC PVD and ECD techniques, and the thickness ranges from 0.45 μm to 1.95 μm. Furthermore, these films are passivated with a standard SiCN dielectric layer. The impurity content of the Cu ECD films is also modified. Wafer curvature, SIMS, EBSD, and XRD measurements are presented. It is observed that at lower Cu film thicknesses there is an "anomalous"shape of the stress-temperature hysteresis loop [5], which is not present at higher film thicknesses. Also, the presence of impurities at the PVD and ECD interface decreases the ''anomalous'' shape of the hysteresis loop. It is observed that repeated thermal cycling of up to 400 °C does not markedly change the texture of these self-annealed films. In addition, Cu grain size measurement results will be presented as a function of thermal cycling, and the grain size is discussed as a function of film thickness. [1] W. D. Nix, Metall. Trans. A 20A, 2217 (1989) [2] S. Kordic, R. A. M. Wolters, and K. Z. Troost, J. of Appl. Phys. 74, 5391 (1993) [3] J. B. Shu, S. B. Clyburn, T.E. Mates, and S. P. Baker, J. Mater. Res. 18 (9), 2122 (2003) [4] Y. L. Shen and U. Ramamurty, J. Vac. Sci. Technol. B 21 (4), 1258 (2003) [5] S. P. Baker, R.-M. Keller-Flaig, and J. B. Shu, Acta. Mater. 51, 3019 (2003)

O4.6

A Model for Curvature in Epitaxially-grown Heterostructures. Ganesh Vanamu[1], Tariq A. Khraishi[2] and Abhaya K. Datye[1]; [1]Chemical and Nuclear, University of New Mexico, Albuquerque, New Mexico; [2]Mechanical Engineering Department, University of New Mexico, Albuquerque, New Mexico.

Growth of lattice mismatched films creates bending in the whole structure. There has been great interest in the study of these curvatures in epitaxially-grown materials. First, stress and strain fields can be determined using curvature measurements of the multilayered system. Second, there is a need to decrease the curvature in a heterostructure as it could pose a problem for device fabrication. An analytical solution for the radius of curvature produced by stresses developed in growing lattice mismatched materials has been obtained. The analyses were based on beam bending theory and strain partitioning theory introduced by our group earlier [1]. The expressions for radius of curvature were obtained for a two-layer heterostructure. The variation of the radius of curvature with the relative thicknesses, relative lattice constants, and relative elastic constants of the layers was determined. A specific application of the model to a SiGe system is provided. The model was verified by applying it to a symmetric tri-laminate structure. The above model can also be extended to determine the curvature for multi-layered heterostructures. REFERENCES: 1. D. Zubia, S. D. Hersee, T. A. Khraishi, Appl. Phys. Lett. 80, 740 (2002).

O4.7

Investigation of Thin Film Elastic Properties by in situ Tensile Testing in a X-Ray Diffractometer. Damien Faurie, Pierre-Olivier Renault, Eric Le Bourhis and Philippe Goudeau; Laboratoire de Metallurgie Physique, Universite de Poitiers, Futuroscope-chasseneuil, France.

Polycrystalline thin solid films exhibit physical, chemical and mechanical properties which can differ from their bulk counterparts. Thin films elaborated by physical vapour deposition can possess a microstructure with high volume proportion of surface and interface atoms, high defect density and preferential orientation (texture). This particular microstructure may induce noticeable modifications of the elastic properties. Moreover, because of the typical thickness of solid films, dedicated testing techniques with a small probe size have to be developed to study the mechanical properties. Therefore, we have developed an in situ tensile tester in a four-circle goniometer on DW22 beam line (LURE facility, France) [1]. The X-ray strain analysis is based on the classical sin2Ψ method, which has been extended here to strongly textured thin films that are composed of elastically anisotropic materials, using the crystallite group method. Preliminary works allowed us to determine elastic constants of 700 nm thick gold films deposited onto polyimide (Kapton) substrate. We discuss the grain-interaction models, appropriated to the diffraction strain analysis of textured thin gold films. ref [1] P.-O. Renault, E. Le Bourhis, P. Villain, P. Goudeau, K.F. Badawi, D. Faurie, Applied Physics Letters 83 (2003) 473

O4.8

A Microtensile Set-up for Characterising the Mechanical Properties of Thin Films. Brigita Cyziute[1], Liudvikas Augulis[1], Joel Bonneville[2], Philippe Goudeau[2], Sigitas Tamulevicius[1] and Claude Templier[2]; [1]Physics, Kaunas University of Technology, Kaunas, Lithuania; [2]Physics, University of Poitiers, Futuroscope Chasseneuil, France.

A computer control deformation set-up has been specifically developed for measuring the elastic and plastic properties of thin films. It combines a piezo-actuated microtensile testing device, based on an original tripod design, with an optical image acquiring and analysis system to measure specimen elongation. The displacement field is determined by using the digital image correlation method. A main advantage of using this technique is that no patterning or marking of the specimen surface is needed. Displacements can be measured at various spots of the film surface, which in practice allows for the evaluation of the Young's modulus and Poisson's ratio. Tensile forces are directly measured with a miniature load cell. Deformation experiments are performed at constant strain-rate with a precise monitoring of the voltage ramp applied to the piezo-actuator. The paper will be partly devoted to present the experimental set up. Preliminary tensile tests have been carried out on 10 micrometers thick aluminium sheets of commercial purity and on polymer foils with thickness of 50 and 75 micrometers. The Young moduli, which are deduced from the stress-strain curves, are in fair agreement with reported bulk average values. The results confirmed the ability of the equipment for the measurements of very small load and displacement levels, which are a prerequisite for such type of investigations. Work is in progress to use this microtensile set up for studying the mechanical properties of free standing thin films of pure copper, as well as aluminium coated polymer foils. Particular attention will be paid to actually characterise the transition between micro- and macro-plastic domain by performing transient tests for evaluating the corresponding activation parameters.

O4.9

Characterization of Stress Relaxation, Dislocations and Crystallographic Tilt Via X-ray Microdiffraction in GaN(0001) Layers Grown by Maskless Pendeo-Epitaxy. Rozaliya I. Barabash[1], Gene E. Ice[1], Wenjun Liu[1], Sven Einfeldt[2], Detlef Hommel[2], Amy M. Roskowski[3] and Robert F. Davis[3]; [1]Metals and Ceramics Div., Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Institute of Solid State Physics, University of Bremen, Bremen, Germany; [3]Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

Intrinsic stresses due to lattice mismatch and high densities of threading dislocations and extrinsic stresses resulting from the mismatch in the coefficients of thermal expansion are present in almost all III-Nitride heterostructures. Stress relaxation in the GaN layers occurs in conventional and in pendeo-epitaxial films via the formation of misfit dislocations, domain boundaries, elastic strain and wing tilt. Polychromatic X-ray microdiffraction, high resolution monochromatic X-ray diffraction and finite element simulations have been used to determine the distribution of strain, dislocations, sub-boundaries and crystallographic wing tilt in uncoalesced and coalesced GaN layers grown by maskless pendeo-epitaxy. An important parameter was the width-to-height ratio of the etched columns of GaN from which the lateral growth of the wings occurred. The strain and tilt across the stripes increased with the width-to-height ratio. Tilt boundaries formed in the uncoalesced GaN layers at the column/wing interfaces for samples with a large ratio. Sharper tilt boundaries were observed at the interfaces formed by the coalescence of two laterally growing wings. The wings tilted upward during cooling to room temperature for both the uncoalesced and the coalesced GaN layers. It was determined that finite element simulations that account for extrinsic stress relaxation can explain the experimental results for uncoalesced GaN layers. Relaxation of both extrinsic and intrinsic stress components in the coalesced GaN layers contribute to the observed wing tilt and the formation of sub-boundaries.

O4.10

High-Cycle Fatigue Testing of Micro/nano-Scale Silicon Nitride Thin Films Using a Novel Mechanical-Amplifier Actuator. Wen-Hsien Chuang[1], Rainer K. Fettig[2] and Reza Ghodssi[1]; [1]Electrical and Computer Engineering, University of Maryland at College Park, College Park, Maryland; [2]NASA Goddard Space Flight Center, Greenbelt, Maryland.

We report the design, fabrication, and testing of a novel electrostatic mechanical-amplifier actuator for fatigue study of micro/nano-scale silicon nitride thin films. Currently, MEMS-based microshutter arrays are being developed as programmable field selectors on NASA's James Webb Space Telescope. The microshutter arrays are made of silicon nitride thin films that require 10^5 life-cycles in outer space; thus, a complete understating of mechanical properties and reliability of silicon nitride is necessary. Our group has developed a resonant technique and a bending approach of T-shaped cantilevers to obtain Young's modulus and fracture strength of silicon nitride thin films. However, it is difficult to apply high cyclic loadings to these cantilevers to study fatigue property and current techniques, such as circular comb-drive actuators, cannot be used for insulating materials. As most electrostatic MEMS devices require high operation voltages, the mechanical-amplifier actuator was designed based on the mechanism of vibration amplification. This device consists of two resonators connected serially with one common torsion bar. Electrostatic energy is pumped to the first resonator via a small controllable gap between electrodes and then transferred to the second resonator which moves freely with the help of the common torsion bar. When the frequency of the pumped energy matches the resonant frequency of the second resonator, large vibration movement of the second resonator can be obtained due to a high quality factor inside a vacuum testing chamber, while keeping the vibration of the first resonator small. The stress amplitude of the second resonator on the torsion bar can then be controlled by the frequency and amplitude of the input electrostatic energy to study fatigue property of the torsion bar on a micro-meter scale. To further understand the fatigue property of silicon nitride thin films on a nano-meter scale, a modified mechanical-amplifier actuator was designed with two torsion bars (instead of one) and tensile samples (200 nm in width). The dual-bar configuration used here is to increase longitudinal stress during rotation of the torsion bars. In addition, one suspended beam is utilized between the torsion bars and the tensile samples to convert torsional stress into tensile stress. According to the above-mentioned operation principle, the tensile stress on the tensile samples can be controlled by the frequency and amplitude of the input electrostatic energy. From our test results, the fracture strength of silicon nitride thin films increases from 6.6 GPa on micro-scale to 7.8 GPa on nano-scale. A time-delay failure was observed on nano-scale tensile samples when testing at stress amplitude over 5.5 GPa. However, the fatigue failure did not occur on the micro-scale torsion bar even up to 10^9 cycles. This can be attributed to the difference in surface conditions and pre-stress status of these two devices.

O4.11

Mechanical and Structural Characterization by X-ray Diffraction in Suspended Bilayer Structure for MEMS Applications. Philippe Goudeau[1], Nobumichi Tamura[2], Sebastien Rigo[3], Talal Masri[3], Jacques-Alain Petit[3] and Jean-Michel Desmarres[4]; [1]LMP, SP2MI, University of Poitiers - CNRS, Futuroscope Chasseneuil, France; [2]ALS, Lawrence Berkeley National Laboratory, Berkeley, California; [3]ENIT, Tarbes, France; [4]CNES, Toulouse, France.

Residual stresses can occur in micro devices during process and operation, giving rise to damage and even to failure. These thermo mechanical stresses are difficult to predict from empirical methods and thus experiments and numerical simulation have to be done together in order to improve our understanding of mechanical interaction at meso scales between materials present in these complex systems. In this paper, a new x-ray diffraction technique has been used for studying residual stresses and microstructure at a micron scale in a 0.56 micron thick gold thin film deposited on a polycrystalline silicon cantilever 20 microns large and 100 microns long. Changing white to monochromatic x-ray beam allows grain selection measurement in the gold layer according to their size: greater than 0.1 micrometer and <111> oriented for white beam and lower (down to a few nanometers) for monochromatic. In both grain populations, the in plane residual stress is tensile and slightly relax along the cantilever beam and becomes nil at the free standing edge. The curvature profile of the deflected beam is measured through the variation, along the cantilever, of the <111> direction due to the curvature of the beam. The obtained results allow validating macro mechanical measurements and analytical and finite element simulations performed on the same systems.

O4.12

Mechanical Properties of *a*-SiC:H Films Grown by PECVD Using 1,3-Disilabutane. Young Kuk Lee and Yunsoo Kim; Korea Research Institute of Chemical Technology, Taejon, South Korea.

Amorphous hydrogenated silicon carbide (*a*-SiC:H) film is of interest as material for MEMs application due to its excellent mechanical and electrical properties. *a*-SiC:H films are usually prepared by PECVD (plasma enhanced chemical vapor deposition) using SiH_4/hydrocarbon gas mixtures. As is well known, SiH_4 gas is very dangerous when exposed to air, consequently the growth equipments are much complicated. A simple way to avoid a explosive silicon source for the deposition of silicon-containing compounds is to use an organosilicon compound that is relatively less active than SiH_4. In this paper, mechanical properties such as nanoindentation hardness and elastic modulus of the *a*-SiC:H films grown by PECVD using an inflammable single source precursor, 1,3-disilabutane, are investigated. The stiffness, the nanoindentation hardness, and the elastic modulus of the films grown at various plasma powers were meaasured by nanoindentation method. Hardness of the film was observed to increase as the plasma power increased, while the elastic modulus was observed to have a maximum value at the plasma power of 10 W. Also the effects of process parameters such as plasma power, growth temperature and work pressure on the chemical state of the each element (Si and C) and surface morphology of the as-grown films are discussed by XPS and SEM studies, respectively.

O4.13

Stress Analysis of Strained Superlattices. Halyna M. Khlyap[1,2] and Roman Peleshchak[2]; [1]Physics, University of Technology, Kaiserslautern, Germany; [2]Physics, State Pedagogical University, Drohobych, Ukraine.

The latest successful development of smart technologies, in particular, molecular-beam epitaxy technique and pulse-laser deposition method, made it possible to manufacture optoelectronic active elements based on semiconductor materials with sufficient mismatch of the lattice parameters. This problem is of special interest for preparing photosensitive devices with strained superlattices. The abstract focuses on the numerical analysis and computational modeling of energy spectra of charge carriers in mechanically strained superlattices based on semiconductor materials from A2B6 and A4B6 (ZnSe, ZnTe and PbS) playing an important part in the optoelectronics design. Computational modeling is settled on the solution of one-dimensional Schroedinger equation and Poisson equation. The simple numerical algorithm is proposed for simulation of the superlattice energy structure in dependence of doping impurity concentration, thickness of the grown layers and their crystallographic orientation.

O4.14

Experimentally and Theoretically Investigations of the Magnetic Phases of Epitaxially Grown EuSe at Low Fields and Temperatures. Klemens Rumpf[1], Petra Granitzer[1], Walter Soellinger[2], Wolfgang Heiss[2] and Heinz Krenn[1]; [1]Institute of Experimental Physics, University of Graz, Graz, Austria; [2]Institute of Semiconductor and Solid State Physics, University of Linz, Linz, Austria.

EuSe is one of the Eu-chalcogenides (EuO, EuS, EuSe, EuTe) Heisenberg antiferromagnets. Due to its metamagnetic behaviour the magnetic phases are more complicated than for example in EuTe and there is an additional antiferromagnetic phase at very low temperatures (below 2 K). This behaviour cannot be solely explained by exchange interaction of nearest neighbors and next nearest neighbors but requires more information about the NNSSNN, NSNS and NNSNNS spin arrangements. Because the nearest and next nearest neighbour exchange constants are nearly cancelled out, higher order interaction becomes important and the biquadratic exchange interaction has also to be taken into account. Our measurements were carried out on an epitaxial grown 2.5 micrometers EuSe film on BaF2. Three regions predicted in the phase diagram of a EuSe bulk crystal are of special interest. For low temperatures (below 1.8 K) and low magnetic fields (below 0.05 T) a NSNS antiferromagnetic (type II) phase occurs. For higher temperatures and fields from 1.8 K to 4.6K and B = 0.1 T to 2.5 T a NNSNNS ferrimagnetic order exists whereas nearby the Curie-temperature of 4.6 K a further antiferromagnetic (type I) phase is formed. The presence of mechanical stress causes fundamental modifications of the magnetic phases. Such a strong mechanical strain is generated in epitaxial layers on substrates with a different lattice parameter like in the investigated sample of 2.5 micrometers EuSe on BaF2. The experimental data show that Mean Field calculations fail on this system. For example the high temperature-fit from 20 K to 200 K demonstrates the difference between Curie-temperature and paramagnetic Curie-Weiss temperature. In addition the determination of the Curie-temperature by Arrott-fits is in good accordance with the critical Heisenberg constants (Mean Field constants are not successful) and leads to 4.1 K.

O4.15

Observation of Micro-Tensile Behavior of Thin Film TiN and Au using ESPI Technique. Yong-Hak Huh[1], Dong-Iel Kim[2], Jun-Hee Hahn[1], Gwang-Seok Kim[1], Chang-Doo Kee[2], Soon-Chang Yeon[3] and Yong Hyub Kim[3]; [1]Center for Env. and Safety Measurment, KRISS, Daejon, South Korea; [2]Department of Mechanical Engineering, Chonnam National University, Kwangjoo, South Korea; [3]School of Mechanical and Aerospace Engineering, Seoul National University, Seoul, South Korea.

MEMS technology has been rapidly developed and nano technology is expected to be a core technology in future. Some data on micro-mechanical properties of these MEMS and nano materials would be required for design and evaluation of reliability of these structure and materials. Micro-tensile properties of hard and soft thin films, TiN and Au, were evaluated by directly measuring tensile strain in film tension using the micro-ESPI(electronic Speckle Pattern Interferometric) technique. Micro-tensile stress-strain curves for these films were obtained and the properties were measured. The thin films 1 μm thick were deposited onto the silicon wafers, respectively, and micro-tensile specimens wide 50 and 100 μm for these films were fabricated using micromachining. In-situ measurement of the micro-tensile strain during tensile test was carried out using the subsequent strain measurement algorithm in the ESPI system developed in this study. The micro-tensile curves showed that the elastic property was dominant in TiN thin film and nonlinear behavior including both elastic and plastic property was presented in Au thin film. Furthermore, effect of the dimension of the specimen on the mechanical properties was examined. It was revealed that tensile strengths for both films were slightly increased with increase of the width of the specimen. And, variations of yielding strengths for the thin film Au with change of the dimension were investigated.

O4.16

Investigation of Viscoelastic Properties of Thin Films via Base-Vibrating Cantilever Beams. Tobias Hoechbauer[1], Yun-Che Wang[1], John Greg Swadener[1], Tim Darling[2], Richard Hoagland[1], Xinghang Zhang[1] and Amit Misra[1]; [1]MST-8, Los Alamos National Laboratory, Los Alamos, New Mexico; [2]MST-10, Los Alamos National Laboratory, Los Alamos, New Mexico.

The unique geometry of thin films poses several difficulties to experimentalists in determining their viscoelastic properties, such as specimen alignment, force/deformation sensor calibration and the usual problem among viscoelastic measurement: necessary resolution of phase lag between force and deformation in a moderate frequency range. Traditional methods with magnetic interaction as driving force and laser-based deformation measurement are inadequate since mounting a permanent magnet and mirror on the specimen changes its mechanical boundary conditions significantly when one deals with a typical laboratory sample whose size is about 10 mm x 1 mm x 20 micron. We propose a different approach to overcome these difficulties by driving a specimen being clamped at the top of a bimorph piezoelectric cantilever beam. The specimen behaves as a cantilever beam under based excitation in translation and rotation. The deformation of the specimen is measured by a fiber-optic system, which requires a sufficient index of reflection at the surface of the specimen. At the resonance of the sample, this method resembles the vibrating weed method generally used in the viscoelastic community with driving force at the free end of the sample. However, under large driving amplitudes, our system is a Duffing-like dynamical system, and this provides a unique opportunity to deduce viscoelastic damping (tan δ) and dynamic modulus from the techniques of system identification. Since, essentially, the sample is driven by its own inertia, the low frequency limit in our measurement can be solved by mounting a lumped mass at its free end. With the maturity of magnetron sputtering techniques, this approach enables us to probe the viscoelasticity of well-defined thin films composed of single or multiple layers.

O4.17

High Cycle Fatigue Damage in Thin Cu Films. Dong Wang, Cynthia A. Volkert and Oliver Kraft; Forschungszentrum Karlsruhe, Karlsruhe, Germany.

A number of recent studies have been performed on fatigue of Cu films on polyimide substrates loaded under large strains (so-called low-cycle fatigue). These studies have confirmed that surface extrusions and cracks form in thin films during cyclic loading, although the film thickness and grains are too small to allow for the formation of extended dislocation structures. The intent of the work presented here is to extend these studies to smaller strains (high-cycle fatigue) and to thinner films. The small strain amplitudes used here (<0.1%) are closer to the strains experienced in metal films and small structures during use in most applications. First results on 0.5 and 1.0 μm thick Cu films show that the damage that forms under low strain amplitudes, is not markedly different in nature from that observed at higher strains. Surface extrusions form within individual grains after around 10^5 cycles, often parallel to twin boundaries, and are paired with intrusions at the film/substrate interface. At higher cycle numbers, the extrusions in neighboring grains connect up and become more pronounced in height and extent. Eventually cracks form along the intrusions. The thinner films exhibit the same trend seen in previous studies, namely that the extrusions decrease in extent with decreasing film thickness and the cracks tend to found along boundaries rather than along extrusions. Studies are currently being performed on 50, 100, and 200 nm thick Cu films and these results and a summary of film thickness effects on fatigue damage will be presented.

O4.18

Analysis of Film Residual Stress on a of 4-point Bend Test for Thin Film Adhesion. Sassan Roham and Timothy K. Hight; Mechanical Engineering, Santa Clara University, Santa Clara, California.

The four-point bend (4PB) test has emerged as a method of choice in semiconductor industry for obtaining bimaterial interface adhesion data. When measuring the interface adhesion using 4PB test, it is essential to obtain a crack through the interface of interest. The deposited films, however, posses intrinsic and extrinsic stresses which affect the ratio between energy release rates for interface cracking and crack penetration. Crack penetration and deflection at a bimaterial interface and the role of residual stress has been broadly studied before. However, the results are based on asymptotic analysis regarding interface between two semi-infinite half spaces, where the results do not directly account for boundary conditions and finite size effects of an actual test specimen. In this paper, we look at the role these residual stresses play on the competition between deflection and penetration energy release rates of a bimaterial interface and the extent of which the previous assumption of two semi-infinite media can be accepted.

O4.19

Practical Work of Adhesion of Polymer Coatings Studied by Laser Induced Delamination. Alexander Fedorov, Jeff Th. M. DeHosson, Redmer van Tijum and Willem P. Vellinga; Applied Physics, Materials Science Centre and the Netherlands Institute for Metals Research, University of Groningen, Groningen, Netherlands.

A novel technique aimed at measuring the practical work of adhesion, or work of fracture, of thin polymer coatings on metal substrates is presented. In this technique an infrared laser pulsed beam is used to create an initial blister. Upon increasing the pulse intensity, the size of the blister grows, resulting in further delamination of the film. Similar to the conventional blister test the work of fracture is derived from the blister pressure and the blister height. In this work both parameters were obtained from independent measurements. Measurements were carried out on a number of samples, presenting ECCS steel substrate covered with 20-40 micrometers thick polyethylene terephthalate (PET) film. Depending on the particular coating the measured work of fracture G varied from 2 to 6 J/m2 (with an accuracy of 0.2-0.5 J/m2). We followed two approaches to model the experiments. First, a simple linear elastic model was investigated. The model predicted the values for the blister height and pressure, which were in fair agreement with the experimental results. In order to account for possible plastic deformations, simulations using a finite element model with a mixed mode cohesive zone were carried out. The calculated stress fields were in agreement with those predicted by the elastic model suggesting that the contribution of plastic deformation to the measured work of fracture is rather limited.

O4.20

Stress Characterization and Crack Evolution of Mo Thin Film Deposited on the Large Area Glass in the TFT LCD Process. Yang H. Bae, Chang-Oh Jeong, Je Hun Lee, Beomseok Cho, Shiyul Kim and Soonkwon Lim; Process Development Team, Samsung Electronics Corp., Yongin-City, Gyeounggi-Do, South Korea.

Mo has been widely used as signal lines in TFT LCDs(thin film transistor liquid crystal displays) due to its good adhesion to other thin film layers and lower contact resistance which TCO(transparent conduction oxide) can be operated properly by, although its resistivity is higher than over 4 times as aluminum's. However, there are some problems in using Mo as signal lines in TFT LCDs, which are originated from sputtering Mo. Stress during sputtering Mo gets glasses curved and makes cracks in steps of a circuit. As rapid progress in TFT LCDs demands large size glass over 1m×1m, those problems becomes serious due to a higher stress. In this study, the effects of process parameters such as pressure, power and thickness on the stress of Mo layer deposited on the large area glass over 1m×1m in the mass production will be investigated. Besides, glass sagging phenomena and cracks in the steps will be analyzed by the stress originated in sputtering Mo. Mo layer was deposited on a glass substrate using DC magnetron sputtering in argon discharge with varying the substrate temperature, the chamber pressure and the sputtering power. In order to examine the effect of the stress of the substrate, the active layer, which contains SiNx layer, a-Si layer and n+ a-Si layer, and has a strong compressive stress, was deposited on the glass and then, Mo layer was deposited sequentially. Thin film stress was measured by laser curvature method and glass sagging technique. Using the above process parameters, TFTs in LCD were fabricated and cross sections were observed. Cross sections of TFT structure were observed by SEM (secondary electron microscopy) attached with FIB(focused ion beam) equipment at 20kV. Stress of Mo thin film measured by laser curvature method is highly tensile in all conditions and increases as pressure and thickness of thin film increase, which is similar to the value measured by glass sagging. Stress of Mo thin film deposited on the active layer is also tensile but the value of stress decreases drastically with compensated for tensile stress. When Mo layer was applied to inverted staggered type TFT as a source/drain layer, cracks occurring in the steps were observed frequently. As stress of Mo thin film increases, the number of cracks increases and the size of cracks becomes larger. Especially, the number and the size of cracks are mainly dependent not on the temperature but on the pressure which is mainly attributed to intrinsic stress. Besides, it is found that the geometry of the step strongly affects the occurrence of crack.

O4.21

Strain Relaxation in Si$_{1-x}$Ge$_x$ Thin Films on Si (100) Substrates: Modeling and Comparisons with Experiments. Kedarnath Kolluri[1], Luis A. Zepeda-Ruiz[2], Cheruvu S. Murthy[3] and Dimitrios Maroudas[1]; [1]Chemical Engineering, University of Massachusetts, Amherst, Massachusetts; [2]Chemistry and Material

Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California; [3]IBM Semiconductor Research and Development Center, Hopewell Junction, New York.

Strained semiconductor thin films grown epitaxially on semiconductor substrates of different composition, such as $Si_{1-x}Ge_x/Si$, are becoming increasingly important in modern microelectronic technologies. Establishing process-structure-function relationships for optimizing the mechanical and electronic properties of these semiconductor heteroepitaxial systems requires development of computationally efficient models for prediction of strained-layer stability with respect to misfit dislocation formation and simulation of the strain relaxation dynamics during film growth and post-growth treatment. In this presentation, we report a hierarchical computational approach for analysis of dislocation formation, glide motion, multiplication and annihilation in $Si_{1-x}Ge_x$ epitaxial thin films on Si substrates. The computational hierarchy includes equilibrium Monte Carlo (MC) simulations for compositional relaxation in the epitaxial film in conjunction with energy-minimization calculations for structural and strain relaxation. The above atomic-scale computations are based on rigorous, reliable many-body interatomic potentials and are combined with continuum elasticity and dislocation theory for parameterization of predictive macroscopic models for the onset of dislocation generation and the kinetics of strain relaxation. Specifically, for $Si_{1-x}Ge_x$ epitaxial thin films on Si(100) substrates, a condition is developed for determining the critical film thickness with respect to dislocation generation as a function of overall film composition, film compositional grading, and (compliant) substrate thickness. In addition, the kinetics of strain relaxation in the epitaxial film during growth or thermal annealing (including post-implantation annealing) is analyzed using a properly parameterized dislocation-mean-field theoretical model of plastic deformation dynamics due to threading dislocation loop propagation. The theoretical results are compared with experimental measurements and are used to discuss film growth and thermal processing protocols toward optimizing the mechanical response of the epitaxial film.

O4.22

Comparison Between In-situ Annealing and External Annealing for Barium Ferrite Thin Films Made by RF Magnetron Sputtering. Alaaedeen Abuzir and W. J. Yeh; Physics, University of Idaho, Moscow, Idaho.

Due to their large magnetic anisotropy perpendicular to the film plane, barium ferrite thick films (BaFe12O19) with c-axis orientation are attractive candidates for microwave applications. Barium ferrite thin films on silicon substrates without under layer have been deposited under various conditions by RF magnetron sputtering. The structure of the as-grown films is amorphous. External annealing in air has been done at 800 -900 C for ten minutes to crystallize the films. C-axis oriented films with squareness of about 0.90 and coercivity of about 5KOe are obtained. Thick BaM films with c-axis orientation are difficult to achieve with one single deposition. Multilayer technique looks promising to grow thick films1. The external annealing process is difficult to incorporate with the multilayer procedure. An in-situ sputtering procedure has been developed to obtain films, which can be used as the basic component for future multilayer deposition. Barium ferrites are first magnetron sputtered on bare silicon substrates in Ar + O2 atmosphere at substrate temperature of 500-600 C, the deposition pressure was kept about 0.008 Torr. After the deposition, the temperature of the substrate is immediately increased to about 860 C for ten minutes in 140 Torr of argon (80%) and oxygen (20%) mixture of gas, which was introduced into the chamber without breaking the vacuum. With the in-situ process, c-axis oriented films of 0.88 squareness and coercivity value of about 4.3KOe are obtained. While both annealing methods seem to have the similar effect on the corecivity and squareness at various film thickness. The average value of the saturation magnetization Ms obtained from the in-situ annealing is higher than that from the external one. We have grown films up to 1 micron thickness using the multilayer technique, in which several layers are deposited until the final thickness is reached. After the deposition of each layer, it was in-situ annealed before starting the deposition of the next layer. With the multiplayer technique, coercivity of about 3.0 KOe and average value of the saturation magnetization Ms of about 3.93 K Gauss is obtained.

O4.23

Correlation between Elastic Constants and Magnetic Anisotropy in Co/Pt Superlattice Thin Films. Nobutomo Nakamura[1], Hirotsugu Ogi[1], Teruo Ono[2], Masahiko Hirao[1], Takeshi Yasui[1] and Osamu Matsuda[3]; [1]Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan; [2]Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan; [3]Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido, Japan.

Magnetization direction of ferromagnetic thin films is usually parallel to the film surface because of the shape-magnetic-anisotropy effect. However, it can be perpendicular to the film plane for magnetic-material/noble-metal superlattice thin films. This magnetic property is called perpendicular magnetic anisotropy (PAM) and attracting many attentions because it can be a candidate of extremely high-density magnetic media recording. PMA will appear when total energy of the system takes a minimum with the perpendicular magnetic direction. The total energy consists of magnetocrystalline-anisotropy energy, shape-magnetic-anisotropy energy, interfacial-anisotropy energy, and magnetoelastic-anisotropy energy. However, previous studies could not discuss a cause of PMA quantitatively, because the elastic constants of the superlattice thin films were not measured, keeping one from calculating the magnetoelastic-anisotroy energy. In this study, we measure the anisotropic elastic constants of Co/Pt superlattice thin films deposited on monocrystal silicon substrates by an ultra-high-vacuum evaporation method using two acoustic methods. One is the resonance ultrasound spectroscopy (RUS) coupled with the laser-interferometry method. This method determines thin film elastic constants by measuring the resonance frequencies of film/substrate layered specimen. Although contributions of thin film elastic constants to the resonance frequencies are usually weak, we achieved high accurate measurement with an accuracy of 10^{-4} using a tripod transducer. The measurement accuracy is significantly smaller than the contributions ($\sim 10^{-2}$). Second is the picosecond ultrasound method. Using a high-power short-pulse laser with 400-nm wavelength, we excite longitudinal waves propagating along the film-thickness direction via the thermoelastic effect. The back echoes reflected at the film/substrate interface are detected by the delayed probing pulse laser with 800-nm wavelength. Determined elastic constants show anisotropy between the in-plane and out-of-plane directions, and a correlation with the degree of PMA. We attribute this to large elastic strain at the interfaces and lattice anharmonicity.

SESSION O5: Thin Film Plasticity- Size Effects

Chair: Ralph Spolenak
Wednesday Morning, March 30, 2005
Room 2022 (Moscone West)

8:30 AM O5.1

Investigating Size Effects in Metals using Microcompression Tests. Cynthia A. Volkert, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

An elegant method has recently been developed for performing compression tests on micron sized specimens [1]. The technique involves machining micron-sized columns from the surface region of a sample using a focused ion beam and then compressing the columns with a flat punch in a nanoindenter. This novel and simple approach allows stress-strain curves to be obtained from samples with volumes from one to 500 cubic micrometers. We have applied this method to look for size effects in a number of metals, including single crystal fcc and bcc metals, amorphous metals, and nanoporous Au. The nanoporous Au provides a control test of the method, since its mechanical properties are independent of the column dimensions. As expected, very high yield stresses in the walls of the nanoporous material are inferred from the stress-strain curves, which indicate that dislocation nucleation is constrained by the 20 nm dimensions. The results from single crystal Au columns down to column diameters as small as 0.5 micrometers showed only a weak effect of length scale on mechanical properties. However, single slip localized within a single band was more common in the smallest columns, which suggests that the characteristic slip distance for a dislocation in the Au samples is on the order of a couple microns. A comparison of the Au results with results from other metals indicates that the surface oxide plays an important role by blocking dislocation motion to the sample surface. Results from other metals as well as from columns containing single grain boundaries will also be presented and the effects of surface oxides and constraint effects from the indenter tip and underlying substrate will be discussed in interpreting the size effects. [1] M.D. Uchic, D. M. Dimiduk, J.N. Florando, and W.D. Nix. Science, 305, 986 (2004).

8:45 AM O5.2

The Evolution and Relaxation of Thermal Stress in Thin Gold Films. Linda Sauter[1], T. John Balk[2], Gerhard Dehm[1] and Eduard Arzt[1,3]; [1]Max-Planck-Institute for Metals Research, Stuttgart, Germany; [2]Department of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky; [3]Institut fuer Metallkunde, Universitaet Stuttgart, Stuttgart, Germany.

The thermomechanical behavior of thin metal films on substrates is influenced by numerous parameters including e.g. film thickness, grain size, passivation layers and the presence of interfaces. For this study, gold was chosen to ensure an unpassivated film surface, since gold does not oxidize at elevated temperatures, in contrast to copper and silver. We will report on the behavior of gold films with thicknesses between 50 nm and 2000 nm that were magnetron sputtered, annealed at 500 °C for 30 min and thermally cycled to 500 °C in a wafer curvature apparatus. Despite the heat treatment, the grain size in these films is roughly constant at 100 nm over the entire film thickness range and does not scale with the film thickness. The flow stresses measured at 50 °C following thermal cycling are relatively high at large film thicknesses, compared to other fcc thin film systems, and continue to increase slightly as film thickness decreases. Furthermore, grain boundary grooves and small voids at triple junctions can be found in films down to 100 nm after thermal cycling. With increasing film thickness, the void size increases and hillocks begin to form. Their size exceeds that of the grains by up to a factor of 20. Focused ion beam and scanning electron microscopy images suggest that hillocks initially form at the film surface and subsequently grow both into the film and out of the film surface, thus involving surface and grain boundary diffusion, which is enhanced by the small grain size. This hillock formation mechanism is in contrast to that of films with a natural passivation layer (e.g. aluminum) where hillocks nucleate at grain boundaries and only grow out of the film surface. Along with observations of dislocation-based plasticity, these diffusional processes and their role in the relaxation of stress in unpassivated gold films will be discussed. The results will also be compared to fine-grained metals, since the deformation in thin gold films also appears to be strongly influenced by diffusion and the large grain boundary area.

9:00 AM O5.3

Plasticity and Interfacial Crack Growth in Thin Gold Films.

Megan Cordill[1], Neville Moody[2], David Adams[3], David Bahr[4], Alex Volinsky[5] and William Gerberich[1]; [1]University of Minnesota, Minneapolis, Minnesota; [2]Sandia National Laboratories, Livermore, California; [3]Sandia National Laboratories, Albuquerque, New Mexico; [4]Washington State University, Pullman, Washington; [5]University of South Florida, Tampa, Florida.

The onset of plasticity is an important factor controlling the properties and performance of thin ductile films. It is the critical factor controlling adhesion of thin gold films. Most studies on gold films have focused on relatively thick films and show that fracture energies are quite high due to extensive plasticity. Recent studies show that fracture energies decrease to relatively low values as films become thin. Although thin film energies are relatively low, the energies are fully capable of forming plastic zones yet there is no evidence of ductile fracture processes on the fracture surfaces. Two models have been proposed to explain this behavior. One model assumes no dislocations are emitted from the crack tip creating a dislocation free elastic zone that shields the crack from background dislocation motion (SSV). Another model assumes that dislocations are emitted from the crack and create a dislocation free zone through crack tip shielding (DFZ). These zones form in material with a high density of lattice dislocations, and highlight the long standing question as to what effect do dislocation interactions have on formation of these zones and on crack behavior. To address this question, we used nanoindentation to simulate dislocation emission in thin gold films that exhibit a ductile to brittle transition in fracture behavior with film thickness. During nanoindentation, we monitored material response to determine dislocation interaction effects. At low loads, reverse plasticity led to time dependent recovery in all films tested suggesting that no significant interactions occur between crack tip emitted dislocations and lattice dislocations. These results will be used to show that elastic regions and dislocation free zones form in ductile metal films and lead to brittle fracture in ductile films. The authors gratefully acknowledge the support of Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:15 AM O5.4

Plasticity of Passivated and Unpassivated Ultra Thin Cu Films Measured by an in-situ Synchrotron Technique.

Patric Gruber[1], Jochen Boehm[1], Linda Sauter[2], Ralph Spolenak[3], Alexander Wanner[4] and Eduard Arzt[1,2]; [1]Institut fuer Metallkunde, Universitaet Stuttgart, Stuttgart, Germany; [2]Max-Planck-Institut fuer Metallkunde, Stuttgart, Germany; [3]Labor fuer Nanometallurgie, ETH Zuerich, Zuerich, Switzerland; [4]Institut fuer Werkstoffkunde I, Universitaet Karlsruhe, Karlsruhe, Germany.

The investigation of size effects in the mechanical properties of thin metallic films on the nanoscale lies in the focus of many research groups. Our thermal cycling experiments with polycrystalline Cu films on stiff substrates revealed a new deformation mechanism which is responsible for a plateau flow stress for films thinner than 300 nm. The so called parallel glide mechanism was correlated to constrained diffusional creep, which involves diffusion between the unpassivated film surface and the grain boundaries at elevated temperatures. To better understand the underlying mechanisms, it is advantageous to decouple temperature and stress. Further the presence of a passivation layer is expected to strongly influence the deformation behavior. In this work we perform tensile tests on different Ta/Cu and Ta/Cu/Ta thin film systems on compliant polyimide substrates and determine the evolution of isothermal mechanical stresses in situ by a synchrotron based X-ray diffraction technique. The film thickness of the Ta cap- and interlayers is 10 nm, whereas the Cu film thickness varies between 20 and 3000 nm. Thus stress-strain curves for Cu films down to a film thickness of 20 nm are obtained. Above 300 nm, the room temperature yield strength of passivated as well as unpassivated Cu films increases linearly with decreasing film thickness, typical for deformation by threading dislocations. Below 300 nm Cu thickness both film systems show a clear deviation from this linear behavior. Unpassivated samples reveal a plateau in flow stress similar to thermal cycling experiments. Thus even at room temperature the parallel glide mechanism seems to be active. In the case of passivated films flow stresses are higher and a clear plateau is not evident. Instead, a change in slope is observed in the yield stress vs. inverse film thickness plots. The different behavior of passivated and unpassivated Cu films will be critically discussed by modeling diffusive processes for a room temperature tensile test.

9:30 AM O5.5

How Stretchable Can We Make Thin Metal Films?

Candice Tsay[1], Stephanie P. Lacour[1], Sigurd Wagner[1], Teng Li[2] and Zhigang Suo[2]; [1]Department of Electrical Engineering, Princeton University, Princeton, New Jersey; [2]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Under cyclic stretching, a thin metal film deposited on an elastomeric substrate can in some cases remain electrically conducting at tensile strains up to $\sim$100%. A recent study used finite-element simulation to explore the rupture process of a metal film on an elastomer. It predicted better stretchability on stiffer elastomeric substrates [1]. We report experiments designed to verify this prediction. The stiffest elastomers available have Young's moduli of $\sim$200 MPa. Spinnable precursors for thin silicone elastomers with such a high modulus are available. For easier handling of these thin layers, we spin the $\sim$10-mm thick stiff silicone elastomer on a 1-mm thick membrane substrate of polydimethylsiloxane (PDMS), a compliant elastomer with Young's modulus of $\sim$ 3 MPa. Stripes of metal film of 5-nm chromium and 25-nm to 100-nm gold (Au) are fabricated either on top of the stiff layer spun onto the soft membrane substrate, or are sandwiched at the interface between the two elastomers. Given the large compliance of the PDMS membrane, these samples behave like metal films attached to the stiff elastomer alone. So far we find that when the metal film (25-nm thick, 600-mm wide Au) is sandwiched between the stiff and compliant elastomers, it retains electrical conduction at 80% elongation, which is higher than the elongation achieved when attached to the 3-MPa PDMS alone. But when the metal film (30-nm thick, 600-mm wide Au) is deposited on top of the elastomers, it remains conducting up to just 8% elongation. These results suggest that, in addition to the stiffness of the elastomeric substrate, the position of the metal film (i.e., top or sandwich configuration) also plays a large role in determining its stretchability. To obtain further information about the mechanism and limit of stretchability, we are studying the effect of film thickness on the maximum elongation. At the Symposium we will give a brief overview of reversibly stretchable metallization, report the preparation of the composite substrates and metallization, and describe the effects of metal film configuration and thickness on electrical conduction under stretching. [1] Teng Li, Zhenyu Huang, Z. Suo, Stephanie P. Lacour, Sigurd Wagner, Appl. Phys. Letters, vol. 85, No. 16, 3435-3437 (2004)

9:45 AM O5.6

An Investigation of Film Thickness on Mechanical Properties of Face Centered Cubic Thin Films on Silicon Substrates.

Yifang Cao[1], Zong Zong[1], Derek Nankivil[2], Seyed Allameh[1] and Wole Soboyejo[1]; [1]Princeton Institute of Materials Sciences and Engineering (PRISM); Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey; [2]Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, Florida.

This paper presents the results of an experimental study of the effects of film thickness on the mechanical properties of face centered cubic thin films that are relevant to microelectronics and microelectromechanical systems. The deformation behavior of e-beam deposited Au, Ag and Ni films on silicon substrates is studied using nanoindentation techniques. The studies show that film hardness is strongly dependent on film thickness and indentation size. The results are then interpreted within the context of strain gradient plasticity theories and mechanics models for the assessment of substrate effects. The measured film moduli are shown to be consistent with film microtexture. Finally, the amount of material pile up is shown to increase with decreasing film thickness, for a given ratio of indentation depth to film thickness. The implications of the results are discussed for the modeling of film deformation and he mechanical behavior of small structures.

SESSION O6: Thin Film Plasticity- Creep
Chair: Marc Legros
Wednesday Morning, March 30, 2005
Room 2022 (Moscone West)

10:30 AM O6.1

Evolution of Stress-Induced Hillocks in Pure Al Films and Lines on Glass Substrate. Young-Chang Joo and Soo-Jung Hwang; Materials Sci. & Eng., Seoul National University, Seoul, South Korea.

During fabrication processes of integrated circuits, interconnect materials are subject to a number of thermal cycles. Differences in thermal expansion coefficients between the various materials in the integrated circuits give rise to a large thermal stress, which results in hillock or whisker formation. Hillocks can bring about excessive surface roughness of the film and interfere with the lights used in the photolithography steps to result in the irregular geometry of the interconnects. Hillocks can also make the dielectric films isolating the metal lines crack to result in inter-metal-level electrical short circuits. Thus understanding and controlling the hillock formation is important to obtain highly-reliable Al interconnects. In this work, we studied the hillock formation of pure Al films, which gains increasing attention for interconnect materials of the thin film transistor-liquid crystal displays (TFT-LCD's). Pure Al films were deposited using the sputtering method to have a thickness ranging from 2500 Å to 10000 Å on a Mo barrier film (500 Å). The substrate material was either glass or Si. A 500-Å-thick Mo capping layer was deposited on some samples. The Al films was annealed at various temperatures from 200 to 400°C and observed using the SEM and the TEM. The average number and the median size of hillocks per unit area were measured using an image analyzer software program that could recognize hillocks from the SEM plane-view images. The orientation of each hillock was identified using the high-resolution electron back-scattered detector (HR-EBSD). We found that the average number of hillocks per unit area decreased and the median size increased with the thicker Al films. SEM observation revealed that there were various types of morphology of stress-induced damages; faceted hillock with poly-atomic steps, rounded hillock and whisker like hillock. From those morphological characteristics, we found that a hillock is formed both by the grain-boundary diffusion and by the dislocation-mediated process. The orientation analysis also showed that hillocks were composed of mainly (110)- and/or (100)-oriented grains. The mechanism responsible for the formation and growth of hillocks are discussed based on the results of both the in-situ SEM observations and the measurements of stress relaxation during isothermal annealing.

10:45 AM O6.2

Driving Force for Hillock Formation in Oxide-Capped Aluminum Thin Films on Sapphire. Jeffrey M. Biser, Sreya Dutta, Helen M. Chan and Richard P. Vinci; Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania.

Sapphire (single-crystal Al_2O_3) is an attractive substrate option for the class of III-V semiconductors, in particular gallium nitride (GaN), which has attracted much attention in recent years as a base material for solid-state laser devices. Our recent work has shown the feasibility of a low-cost process for producing pristine sapphire surfaces. Using a sapphire substrate with a relatively poor surface finish as the starting material, we begin by depositing an Aluminum thin film, anneal to Grow a polycrystalline Oxide layer, and follow this with Grain growth at higher temperature, resulting in solid-state conversion into single crystal sapphire. The surface produced has been shown by AFM to have an RMS roughness reduced from roughly 10 nm pre-process to <1 nm. This procedure has been designated the AGOG process. One of the critical problems that occurs during this process is the appearance of hillocks during the first anneal due to thermal stresses. We have had success in preventing such hillock growth, while maintaining the convertibility of the films to sapphire, by forming aluminum oxide capping layers of varying thickness via reactive sputtering and anodization. However, the success of this approach does not uniquely identify the mechanism for hillock suppression. A number of different mechanisms have been proposed for similar materials systems. Two scenarios appear most likely: 1) the presence of the oxide overlayer prevents the metal film from ever experiencing compressive stresses at the annealing temperature, thereby removing the driving force for hillocking, or 2) assuming the film does in fact go under compression, the capping layer may simply be sufficiently thick to act as a mechanical barrier to hillocking. The goal of this study is to separate out the two possibilities mentioned above. For films capped with both anodic and sputtered oxides of varying thickness, we have performed x-ray diffraction stress measurements in the metal film during a heating cycle from room temperature to 450 °C. By identifying the stress state in the metal film as a function of temperature and oxide thickness, we may both better understand the mechanisms behind our approach toward hillock suppression, and tailor the capping layer thickness for maximum efficiency and convertibility. Hillock counting and characterization is performed through electron- and optical microscopy with digital image processing. Sapphire conversion is checked through EBSD/OIM and TEM.

11:00 AM O6.3

Microtensile Testing of Gold and Gold-Vanadium Thin Films at Elevated Temperatures. Ming-Tzer Lin[2], Paul El-Deiry[3], Richard Chromik[4], Nicholas Barbosa[3], Walter Brown[3], Terry J. Delph[1] and Richard Vinci[3]; [1]Department of Mechanical Engineering & Mechanics, Lehigh University, Bethlehem, Pennsylvania; [2]Institute of Precision Engineering, National Chung Hsing University, Taichung, Taiwan; [3]Dept. of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania; [4]Naval Research Laboratory, Washington, District of Columbia.

We report here on the results of a series of microtensile tests of gold and gold-vanadium thin films carried out at room and at temperatures up to 400 C. Specimens were fabricated by sputtering gold onto a thin titanium adhesion layer on a silicon nitride coated silicon wafer, and then using standard wet etching techniques to pattern a series of microtensile specimens in the gold/titanium metal film. The underlying silicon substrate was then chemically etched away under the gage section of the specimen, followed by dry etching to remove the silicon nitride and the titanium. This left a free-standing gold test specimen approximately 600 μm long with a width of 100 μm and a thickness of approximately 1 μm. The titanium remained under the gold on the region outside the gage section to maintain good adhesion with the substrate that would subsequently be gripped for tensile testing. Gold-vanadium specimens of similar dimensions were prepared by co-sputtering, with vanadium concentrations ranging from 3% to 5% atomic percent. The specimens were annealed in air at 400 C for 3 hours before mechanical testing. Testing was carried out in a specially designed microtensile device, designed to accommodate a small split box oven. Loading was applied using a piezoelectric actuator with 0.1 μm resolution. Loads were measured using a double-cantilever beam load cell with a resolution of less than 0.1 mN and a compliance of 30 mN/μm. The entire testing apparatus was mounted inside a thermally insulated enclosure, within which the temperature was controlled by cooling water to within 0.3 C. This had the effect of limiting thermally induced drift in the system, and made it feasible to conduct elevated temperature relaxation tests with durations on the order of several minutes. A typical test history involved constant strain rate straining to a predetermined strain level, a constant strain relaxation period of 20-120 sec duration, then constant strain unloading followed by a zero load hold period. This loading cycle was repeated three to four times. Strain rates for the loading/unloading phases were 3.3 x 10-4 /sec or 3.3 x 10-3 /sec. Both gold and gold-vanadium specimens demonstrated an increase in effective Young's modulus with increasing strain rate. This strain rate sensitivity indicates the presence of inelastic deformation during the loading/unloading phases. Tensile yield stresses were increased both by increased strain rates and by the addition of vanadium. In addition, stress relaxation tests conducted at 400o C on gold-vanadium specimens at constant strain demonstrated much less relaxation than did pure gold specimens under comparable strain histories. We conclude that the addition of vanadium to gold generally suppresses inelastic deformation.

11:15 AM O6.4

Characterization of Structural and Mechanical Properties of NiTi Shape Memory Thin Films for Micro Actuators. David Getchel and Richard Norman Savage; Materials Engineering, Cal Poly State University, San Luis Obispo, California.

Microactuators fabricated with NiTi thin films can take advantage of this materials large energy density (~ 5-10 joule/cm^3) and high strain recovery (~ 10%). MicroElectroMechanical System (MEMS) devices designed with these actuators can serve as bio-sensors, micro-fluidic pumps or optical switches. However, the fundamental mechanical properties stemming from crystalline structure of these super elastic or shape memory NiTi films have not been fully characterized. Understanding the inter-relationship of crystalline structure, film stoichiometry and phase transformation temperature is crucial when designing a MEMS actuator. In addition, measurement of force displacement curves for both the Martensite and Austenite phases of NiTi will provide fundamental material properties for these films. NiTi films were deposited using a DC Magnetron co-sputtering processes. Film compositions were studied using energy-dispersive x-ray spectroscopy (EDS), which indicated that vacuum annealing was necessary to avoid Ti depletion due to oxidation. The impact of annealing conditions on crystal structures and grain sizes were studied by grazing incidence x-ray diffraction (GIXD) and electron backscattering diffraction (EBSD). By examining the A(110) XRD peak (42.5° 2θ), the phase transformation temperature cycle was examined from 60- 100 ^{o}C. Results to date indicate NiTi films with 50.1 to 50.7 at% Ti are capable of shape memory phase transformation. Test structures, fabricated by patterning NiTi films using optical lithography and wet etching, enabled force-displacement profile characterization. Sputter deposited chromium layers promoted NiTi film adhesion to the silicon substrate and prohibited Ni diffusion during annealing. Both cantilever and fixed beam test structures, ranging from 50 x 100 to 100 x 500 microns were characterized. A profilometer measured beam deflection (with ~ 1.5 Å resolution) while applying a constant force (0.05-30 mg) as the film was cycled through its phase transformation temperature using joule heating. From these measurements the strength and strain for both the Austenite and Martensite phases of NiTi thin films was determined.

11:30 AM O6.5
Influence of Gas Atmosphere on Thin Metal Film Plasticity. Thomas Wuebben, Gerhard Dehm and Eduard Arzt; Arzt, Max-Planck-Institute for Metals Research, Stuttgart, Germany.

Heterogeneous catalytic reactions at metal surfaces are of major interest in industrial process control. However, despite this technique has been widely used in large scale production for decades, an understanding on the atomic level is still lacking. This is mostly due to the complicated scenario at the interface during the reaction. This involves chemical parameters like binding energies and enthalpies as well as geometrical properties like molecule sizes, lattice constants and local stresses. One of such reactions is the oxidation of methanol (CH3OH) to formaldehyde (CH2O) on a copper surface at temperatures of about 250°C. In this case, three reaction paths are possible, of which the dehydration, i. e. $2CH_3OH+O_2$ -> $2CH_2O+2H_2O$ implies the adsorption of methanol and oxygen at the copper surface to form the reaction products. However, the reaction kinetics observed in laboratory experiments differ strongly from industrial process experience. The aim of our project is to investigate the role of elastic strains in the copper lattice during the catalytic reaction. It has been shown in theoretical calculations that a lattice constant increase by about 1% as well as high local stresses can alter the binding energies and thus the reaction kinetics. However, the flow stress of bulk copper is too low to achieve sufficiently high strains or stresses. This problem can be overcome using thin Cu films, since their flow stress decreases significantly with decreasing film thickness. To generate and measure the stress, we applied the wafer curvature technique. Thin Cu and Pd films were deposited on non-metallic substrates. Due to thermal mismatch the metal film is strained when the sample is heated, leading to a bending of the film-substrate composite, measured by a laser scanning technique. Above a critical temperature the flow stress is reached and the film deforms plastically. This leads to a hysteresis in the stress-temperature curve. Thus, by heating to different maximum temperatures, the strain at a given temperature can be varied. Another method to vary the stress at the catalytic temperature is to vary the film thickness, since the flow stress depends inversely on this parameter. We will present first results on the influence of different ambient conditions on film stresses in thin metal films measured with the wafer curvature technique.

11:45 AM O6.6
Laser Lateral Crystallization of Thin Metallic Films on SiO_2. James E. Kline and John P. Leonard; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Today there are significant new materials challenges relating to modification of microstructures in metallic thin films for advanced device applications. Examples include the control of polycrystalline microstructure and interface morphology in copper-based interconnects, as well as the formation of specialized electrode attachments to oxides in acoustic wave devices, MEMS and sensors. Although conventional rapid solidification processing (RSP) has long been recognized as a powerful and flexible technique to obtain refined microstructures and non-equilibrium compositions in metals, it has been largely incompatible with– and absent from– thin film device processing. Pulsed laser irradiation, however, is an alternative route to RSP in thin film materials, and has been successfully applied to the crystallization of Si on amorphous substrates. Using pulsed excimer laser melting, we demonstrate the formation of laterally solidified ultra-large grains in 200nm Cu, Au, and Cr sputtered films on an amorphous SiO_2 substrate. Lateral solidification of metals is found to be possible only when several requirements are met, including 1) Complete melting of the film in a spatially isolated (narrow line) region, 2) Encapsulation with a SiO_2 capping layer to suppress the dewetting behavior commonly observed in molten metal films, 3) Avoidance of nucleation to allow lateral solidification to proceed. Details of the irradiation parameters will be presented, along with estimates of interface velocities and temperatures. TEM analysis of post-solidified microstructures will be used to characterize the defects and crystal morphology of the rapid laterally solidified films produced by this technique.

SESSION O7: Thin Film Plasticity- Modeling
Chair: Thomas Buchheit
Wednesday Afternoon, March 30, 2005
Room 2022 (Moscone West)

1:30 PM O7.1
Discrete Dislocation Study of Freestanding Thin Films. Lucia Nicola[1,2], Erik Van der Giessen[1] and Alan Needleman[2]; [1]Materials Science Center, University of Groningen, Groningen, Netherlands; [2]Division of Engineering, Brown University, Providence, Rhode Island.

Vlassak and co-workers at Harvard University employ a bulge test machine to subject thin films to tension under plane strain conditions. By polishing polycrystalline films down to various thicknesses, they have obtained the dependence of the plastic response on film thickness, in the range from 1 to roughly 4μm independent of grain size. In addition to bare copper films, they have also studied films that are passivated by a very thin layer of nickel. Unloading and partial inverse loading has revealed a strong Bauschinger effect in passivated films. We report on discrete dislocation plasticity calculations aimed at complementing these experiments. Motivated by the above-mentioned experiments, we employ a two-dimensional model of a film with columnar grains, under plane strain conditions perpendicular to the plane. The film is modeled as an infinite array of rectangular grains, with a certain periodicity in the film direction. Each grain in the unit cell has three slip systems according to two-dimensional rojection of cubic crystals, and its orientation is random. Plastic deformation occurs by the nucleation and motion of edge dislocations, treated as line singularities in an elastic continuum. Periodic boundary conditions and traction-free conditions at the film surfaces are incorporated through a finite-element image solution. We argue that a meaningful comparison with real three-dimensional free-standing polycrystal films requires that additional constraints be imposed to mimic the out-of-plane interactions between grains. Results for varying film thickness, at constant grain size, are presented for a set of parameter values that have been fitted to the Vlassak et al. experimental data. The predicted film thickness effect is shown to be due to the piling-up of dislocations against the impenetrable passivation layer. This also provides an explanation for the origin of the Bauschinger effect upon unloading.

1:45 PM O7.2
Direct Dislocation Dynamics Simulation of Annihilation Radius in Thin Films. Meijie Tang, Lawrence Livermore National Lab., Livermore, California.

In heteroepitaxial thin films, the threading dislocations interact with each other through a series of annihilation reactions to reduce their density as film thickness increases. Several models were able to predict the well established 1/h behavior [1]. However, a crucial parameter that was often treated unknown is the annihilation radius betwen a pair of anti-parallel dislocations. The annihilation distance is determined by the balance between the elastic interaction (i.e., the Peach-Kohler force) between them and the lattice resistance. With the presence of free surfaces, the elastic stress fields can be significantly altered. Depending on the relative orientation between the dislocation and the free surface, there is no easy analytical solution to calculate the interaction force between two dislocations inside a thin film. We developed a dislocation dynamics (DD) method that was coupled with a finite element model (FEM). A practical and robust algorithm is implemented in this coupled DD-FEM approach to treat image stresses at the free surfaces. In this work, the coupled DD-FEM method is used to calculate the annihilation distance of a pair of inclined dislocations in a metallic system by performing direct DD simulations. The results show strong dependence on the film thickness. While both the line tension and the image stresses play important roles, the image stresses significantly reduce the annihilation distance. The work is performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. [1] A. E. Romanov, W. Pompe, G. E. Beltz, J. S. Speck, Appl. Phys. Lett. 69 (1996) 3342.

2:00 PM O7.3
Comparison of Dislocation-SFT Interactions in Bulk and Thin Film Materials. Yury Osetskiy[1], Roger E. Stoller[2] and Steven Zinkle[2]; [1]Computer Sciences and Math, ORNL, Oak Ridge, Tennessee; [2]Metals and Ceramics, ORNL, Oak Ridge, Tennessee.

Thin-film in-situ straining experiments are often used to study details of dislocation-obstacle interactions. These mechanisms are used then in interpretation of mechanical testing of bulk samples. In this paper we present the results of large-scale atomic-level modeling of screw dislocation dynamics in bulk Cu and thin films with free surfaces. The case considered as an example is related to quenched and irradiated fcc metals with a low stacking fault energy when the dominant microstructure is a high number density of stacking fault tetrahedra (SFTs), which is vacancy-type defect with a rather high stability. We demonstrate that cross-slip is an important mechanism of dynamics of screw dislocations and interaction with SFTs and the results of this interaction i.e. critical resolved shear stress, microstructural changes, etc. depend on whether bulk metal or thin film are considered, temperature and strain rate. The results obtained are used in interpretation of experimental observations in irradiated and in-situ strained metals.

2:15 PM O7.4

Dislocation Evolution in Thin Film-Substrate Heterostructures. Lizhi Sun and E. H. Tan; University of Iowa, Iowa City, Iowa.

A novel dislocation dynamics framework is developed to simulate dislocation evolutions in thin film heterostructures. It is based on 3-D dislocation motion together with its physical background by adding the solid viscous effect. As the numerical simulation results demonstrate, this new model completely solves a long-standing paradoxical phenomenon with which the simulation results were dependent on dislocation-segment lengths in the classical discrete dislocation dynamics theory. The proposed model is applied to simulate the effect of dislocations on the mechanical performance of thin films. The interactions among the dislocation loop, free surface and interface are rigorously computed by decomposing this complicated problem into two relatively simple sub-problems. This model is allowed to determine the critical thickness of thin films for a surface loop to nucleate and to simulate how a surface loop evolves into two threading dislocations. Furthermore, the relationship between the film thickness and yield strength is constructed and compared with the conventional Hall-Petch relation.

2:30 PM *O7.5

Deposition and Characterization of Ti-Ni-Pd and Ti-Ni-Pt Shape Memory Alloy Thin Films. Greg P. Carman, Daniel Shin and K. P. Mohanchandra; MAE, UCLA, Los Angeles, California.

Thin films of Ti-Ni-Pd and Ti-Ni-Pt shape memory alloys are produced by d c magnetron sputtering technique on (100) Si substrates. Targets with different compositions of Ti-Ni-Pd ($Ti_{54}Ni_{16}Pd_{30}$, $Ti_{54}Ni_{6}Pd_{40}$ and $Ti_{54}Ni_{2}Pd_{44}$) and $Ti_{54}Ni_{26}Pt_{20}$ are used for the present study. Film deposited onto a silicon substrate at ambient temperature is amorphous and *insitu* annealing at 600°C for 1hour crystallizes the film. Film crystalline structure, phase transformation, microstructure and residual stresses are characterized by X-ray diffraction, differential scanning calorimeters (DSC), transmission electron microscope (TEM) and wafer curvature methods. X-ray diffraction data show that the structure of the martensitic phase is orthorhombic (B19). Composition of the films is determined using electron probe micro-analyzer (EPMA). Results indicate that as the Pd content increases to 40at% the transformation temperature A_f, austenite finish temperature, increases up to 425°C. For the Ti-Ni-Pt film, even at 20at% Pt, the austenite finish temperature is 425°C. TEM micrographs show both Ti-Ni-Pd and Ti-Ni-Pt films have well defined twin structure at ambient temperature. Experimental data also demonstrate that all the films fabricated exhibit the classic shape memory effect.

SESSION O8: Novel Testing Techniques
Chair: Thomas Buchheit
Wednesday Afternoon, March 30, 2005
Room 2022 (Moscone West)

3:30 PM O8.1

Effects of Specimen Alignment on the Mechanical Properties of Polysilicon Film. Shin-Woo Kim[1], Chung-Seog Oh[1] and Hak-Joo Lee[2]; [1]Mechanical Engineering, Kumoh National Institute of Technology, Gumi-si, Gyeongbuk, South Korea; [2]Structural Research, Korea Institute of Machinery and Materials, Daejeon-si, South Korea.

The uniaxial freestanding specimens are commonly used to characterize the mechanical properties such as elastic modulus, tensile strength, fatigue strength, etc. for a thin film. Because tensile tests have the advantage of uniform stress and strain fields, which is why they are the most way to determine mechanical properties at larger scales. However, they have disadvantages at smaller scales in that specimen preparation can be expensive and specimen gripping may be difficult. Especially, gripping and alignment are fraught with potential errors. In reality, the elastic modulus, tensile strength, and fatigue behavior are very dependent on not only the fabrication procedures but also the test methods. The aim of this paper is to investigate the effects of specimen alignment on the elastic modulus, tensile strength, and fatigue behavior. The specimens are fabricated at the MEMScAP by the PolyMUMPs process. The gage section is 1 mm long, 2 um thick, and 50 um wide. There are two gold lines, which are 0.25 mm apart, that are the reflective markers for the strain measurement using the ISDG (interferometric strain/displacement gage). A tensile test is preceded to measure the elastic modulus in the elastic range to a fatigue test to assure the specimen alignment. A commercial piezoelectric actuator and a homemade voice coil actuator are utilized for the low and the high cycle fatigue test, respectively. The load is measured by a commercial load cell and controlled by a closed-loop feedback control program during a fatigue test. The elastic modulus is varied from 130 to 160 GPa according to the height difference, which is only 1 micron, between the load line and the specimen centerline. In addition, the tensile strength reaches up to 1.7 GPa. It is very interesting to note that the modulus is very dependent on the specimen alignment but reaches a maximum value of 160 GPa at the best alignment. This fact is applied to find the best alignment before doing a fatigue test. A S-N (stress-life) curve of polysilicon film with the best alignment condition is obtained and compared with the results of other researchers. It should be noted that the S-N curve we obtained shows much higher fatigue resistance than the other results. This implies that the specimen alignment plays a crucial role in doing a fatigue test. The better the alignment, the higher the modulus and tensile strength, and the higher the fatigue strength. The test procedures and some interesting test results will be introduced in detail.

3:45 PM O8.2

Thermal Expansion of Low Dielectric Constant Thin Films by High-Resolution X-ray Reflectivity. Kazuhiko Omote, Rigaku Corporation, Akishima, Tokyo, Japan.

In recent years, new low dielectric constant materials have been considerable interest for reducing dielectric constants of interlayer insulators. For introducing such new materials into microelectronic devices, thermal properties of the film is very important, because of the film will undergo the thermal stresses in the fabricating processes of the devices. X-ray reflectivity (XRR) technique is known to be able to measure density and thickness of thin films very accurately. We are trying to measure density and thickness changing rising to the film temperature by this technique. However, thermal expansion coefficients of materials are typically about $10\hat{(}-5)/K$ and the changing may be less than one percent, even if the temperature is rising 100 degrees. Therefore, we need a very accurate XRR measurement for detecting thermal expansion of the film materials. For this purpose, we have developed a high-precision goniometer and high-resolution crystal beam conditioner and analyzer system. The repeatability of the measurements has been achieved to be within plus minus 0.3 arcsecond. The samples are deposited by CVD method and including very small pores (about one nanometer in diameter). Experiment was carried out in nitrogen atmosphere up to 400 degrees after preheating for evaporating adsorbed water. The data were corrected at both heating and cooling processes for confirming the film materials was not deteriorated. The density and thickness of the film was determined by the least square fitting for minimizing the residual error between the observed experimental data and XRR calculation. The estimated error of the obtained density and thickness are about 0.2% and 0.05%, respectively. From the thickness changing of the film, we could estimate z-direction (normal direction) coefficient of linear thermal expansion, beside from the density changing, we could estimate coefficient of volumetric thermal expansion, independently. We will discuss these obtained values comparing other materials and also discuss the relation between the z-direction linear thermal expansion and the volumetric thermal expansion.

4:00 PM O8.3

Investigation of Local Stress Fields: Finite Element Modelling and High Resolution X-Ray Diffraction. Audrey Loubens[1,2], Christian Rivero[1,3], Philippe Boivin[3], Barbara Charlet[4], Roland Fortunier[2] and Olivier Thomas[1]; [1]TECSEN UMR 6122, Marseille, France; [2]Ecole Nationale Superieure des Mines de Saint Etienne CMP Georges Charpak, Gardanne, France; [3]ST Microelectronics, Rousset, France; [4]CEA Leti, Grenoble, France.

The influence of local stress fields on the electrical properties of Si-based nanostructures is of increasing concern. The experimental evaluation of stresses at the required scale (few nanometres) remains, however, a very challenging task. We propose a non destructive X-ray diffraction technique for local strain measurements using a laboratory radiation source. This technique provides an alternative route to micro diffraction experiments. High resolution X-ray diffraction is used to analyse the diffraction from the periodic strain field induced in silicon by a periodic array. We analyzed arrays of Si3N4 lines (two arrays with the following dimensions: thicknesses: 400 nm and 500 nm, widths: 650 nm and 900 nm, pitches:280 nm and 320 nm) on silicon, and arrays of single crystal Si lines (three different periods: 2,1 and

0.6 micrometers, width: period/2, thickness: 100 nm) etched in SOI (Silicon On Insulator) and capped with SiO2 and Si3N4. Reciprocal space maps were performed around the Si substrate diffraction lines. A Bartels 4 reflections Ge 220 monochromator was used in combination with a 3 reflections Ge 220 analyser. X ray diffraction rocking curves performed on Si 004 and Si 224 reveal distinct superlattice peaks whose spacing is related to the in-plane periodicity. Reciprocal space maps reveal particular intensity distributions caused by the stress gradient in the transverse and perpendicular directions of the lines. Reciprocal space maps obtained by High Resolution X-Ray Diffraction are compared with maps calculated from displacement fields derived from finite element modeling. Finite Element Modeling indicates that the stress induced by the Silicon lines on Insulator in the underneath Si substrate decreases abruptly, on about hundred nanometres, from 300 MPa to few MPa. Very clear superlattice peaks are, however, observed around the bulk Silicon substrate reciprocal lattice nodes, which indicates a great sensitivity of this method to elastic stresses. The influence of the lines aspect ratio on the reciprocal space maps has been studied both experimentally and through modelling. Large variations are observed but the separate influence of each stress tensor component still needs to be identified.

4:15 PM O8.4
Determining Forces of Self-Assembly in Thin Films by measuring Thermal Vibrations. Konrad Thuermer and Norman Bartelt; Sandia National Laboratories (CA), Livermore, California.

Deposition of sulfur onto a monolayer of Ag on Ru(0001) transforms the herringbone pattern of the clean Ag-film into a strikingly regular array of 2D-vacancy islands [K. Pohl et al. Nature 397 (1999) 238]. We have previously shown (Phys. Rev. Lett. 92, 106101-1 (2004)) that this nanometer-scale restructuring proceeds via misfit dislocation reactions. In this talk we will discuss measurements, which show that the arrangement of the dislocations determines the mechanical stability of the final self-assembled structure. In scanning tunneling microscopy image sequences we observe the vacancy island lattice to vibrate on a temperature dependent time scale. The anisotropy of these thermal vibrations allows us to determine the nature of the forces keeping these holes in a well-ordered triangular lattice. Surprisingly, our measurements reveal a significant force component perpendicular to the line connecting a vacancy pair. Using a 2D Frenkel-Kontorova model we can explain the observed anisotropy of the hole-hole interaction as a property of the dislocation network in the Ag film. Substrate-mediated elastic dipole interactions due to variations in surface stress are often invoked to explain self-assembly in thin films. Our measurements rule out the importance of these interactions in this system because they would generate a force between neighboring holes acting only along the connecting line.

4:30 PM *O8.5
Using the Electron Microscope to Explore Reliability in Nanostructured Materials. Eric A. Stach[1,2], D. Ge[2], A. Minor[2], J. W. Morris[3], V. Gopal[1] and V. Radmilovic[1]; [1]School of Materials Engineering, Purdue University, West Lafayette, Indiana; [2]National Center for Electron Microscopy and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California; [3]Department of Materials Science and Engineering, University of California, Berkeley, California; [4]Department of Materials Science and Engineering, Pennsylvania State University, College Station, Pennsylvania.

In this presentation, we will discuss the development and application of a number of novel *in − situ* electron microscopy techniques that exploit the inherent high resolution and dynamic imaging capabilities of the electron microscope to explore mechanical and electromechanical reliability of nanostructured materials. We have built a unique sample holder that allows us to perform nanoindentation of materials inside the transmission electron microscope (TEM). This lets us apply a mechanical force to a particular area of an electron transparent material and observe in real time the internal mechanisms by which the sample responds to the applied load. In the major part of this presentation, we will review our work on model metallic (Al) and semiconducting (Si) material systems, with an emphasis on how nanoscale size effects can fundamentally alter material hardness. In the case of aluminum, we find that as grain sizes shrink, the participation of grain boundaries in the deformation process yields easy dislocation nucleation and thus significant softening of the material. For silicon, the presence of free surfaces associated with small sample changes the predominant deformation mode from one of phase transformation to dislocation plasticity. Finally, we will discuss the development and preliminary application of a new in-situ technique for probing the electromechanical reliability of nanostructures, that of in-situ electrical biasing. Details of a new nanoscale contact methodology based on focused ion beam patterning will be reviewed, and initial results of electromigration in silver nanowires will be presented.

SESSION O9: In-Situ Characterization Techniques

Chair: Andrew Minor
Thursday Morning, March 31, 2005
Room 2022 (Moscone West)

8:30 AM *O9.1
In-Situ TEM Study of Plastic Stress Relaxation Mechanisms in Metallic Films. Marc Legros[1], Gerhard Dehm[2], T. John Balk[3] and Eduard Arzt[2]; [1]CEMES-CNRS, Toulouse, France; [2]Max-Planck-Institut fuer Metallforschung, Stuttgart, Germany; [3]Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky.

The mechanical behavior of metallic films with sub-micron thicknesses brings to front puzzling questions about small scale plasticity and interfaces effects. When bonded to a rigid substrate such as silicon or sapphire, and thermally cycled, metal films (Al, Cu, Au) exhibit an increase of yield stress with decreasing thickness. This effect is weaker for films epitaxially grown on their substrate than for films attached to a substrate previously coated with an amorphous diffusion barrier. Recent in-situ TEM (Transmission Electron Microscopy) experiments on Cu or Al thin films have shown that this amorphous interface can act as a dislocation sink, in a very similar way to free surfaces in free standing films. In the same time, dislocation sources are scarcely observed during in-situ tests, and almost exclusively in the case of an epitaxial interface. Such findings, combined with the lower mechanical resistance of epitaxial films on sapphire, weaken the current "threading dislocations" models. On the other hand, many recent experiments show that substantial diffusional phenomenon take place in these films: grain boundary diffusion (that may trigger zero stress parallel dislocation glide), whisker formation, pipe diffusion. Some of these mechanisms, although difficult to observe dynamically, may relax most of the applied stress. This talk will focus on results obtained in different cfc metals thin films using in-situ and post-mortem TEM and SEM observations. Differences and similarities between free standing and bonded films will be discussed from a microstructural point of view.

9:00 AM O9.2
In-situ Stress Characterization in MEMS Thin Suspended Metallic Membrane. Wei Wei[1], Mark Bachman[2] and Guann-Pyng Li[3]; [1]Integrated Nanosystem Research Facility, ChEMS, UC, Irvine, Irvine, California; [2]Integrated Nanosystem Research Facility, EECS, UC, Irvine, Irvine, California; [3]Integrated Nanosytem Research Facility, EECS, UC, Irvine, Irvine, California.

Foundry CMOS processes are widely adopted for Micro Electro-Mechanical Systems (MEMS) research nowadays. Since these processes are initially developed for electronic devices and properties investigation, the mechanical properties related stability issues of MEMS devices are not always addressed. One of the crucial components in MEMS devices is suspended membrane, metallic or nonmetallic. Such components are in a constant motion under various actuation or stimulation in response to ON and OFF. One of the major failure mechanisms for this type of structure is stress induced fatigue and fracture during cycling loading and unloading. Although a lot of research efforts have been endeavored in applying MEMS structures into a wide range of applications, such as RF communication, chemical and biomedical sensing, and so on, the current understanding of the stress induced device failure mechanisms are still limited. As a result, how to improve the structure properties from mechanical point of view for a better device performance is still an area need further investigation. The first step in tackling the stability issue of MEMS devices with a suspended membrane as a key component is to fully understand the residual stress and stress field under actuations in the membrane. Several approaches have been developed and accommodated, such as bulge test, micro-tensile and micro-bending test, nano-indentation test, and dynamic vibration test. Among these techniques, only nano-indentation test does not require specific specimens measurements. Apparently, nano-indentation test is not an appropriate approach for mechanical testing of suspended structures. Further more, the mechanical properties of MEMS structure, which is normally in the micro-domain, are size-, thickness-, and geometry-related. As a result, in-situ characterization techniques need to be implemented. In this study, suspended aluminum membrane structures are constructed in five steps: silicon dioxide sacrificial layer deposition, aluminum film deposition, film patterning, film selective etching, and sacrificial layer etching. High Resolution X-Ray Diffraction (HRXRD) technique is employed to characterize the suspended aluminum membrane structure. X-Ray beam is confined to around 10 micrometer in dimension and directed to different spots on the membranes. <111> texture is observed from X-ray diffraction pattern in each film deposited using high vacuum thermal evaporation technique. The diffraction peak locations of stressed membranes are compared with an unstressed counterpart and residual stresses are inferred from the lattice constant distortion. Residual stresses in suspended membranes are measured under different device dimensions, film thickness, and geometries. A comparison of residual stress status is also made between suspended membrane and membrane on substrate. Experimental results are also compared with finite element method simulation results to verify the validity of our approach.

9:15 AM O9.3
Nanometrology of Multilayer Polymer Thin Films.
Christopher M. Stafford, Shu Guo and Martin Y. M. Chiang; Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

Nanotechnology promises to revolutionize a growing set of materials applications ranging from electronics to drug delivery to ballistic protection. However, the quest to engineer materials on the nanoscale (e.g., in the form of ultrathin films) is met with the daunting task of measuring the physical and mechanical properties of these systems. Understanding the mechanical properties of nanofilms is especially critical in the fabrication of MEMS, NEMS, and electronic devices. Often, device geometry and function requires multi-layer assemblies. Current methodologies such as indentation can probe the bulk mechanical properties of each material individually but are challenged by thin polymer films as well as multilayered structures. We will discuss the application of our buckling-based metrology to measure the mechanical properties of multilayer assemblies. Multilayer stacks are assembled on PDMS substrates by a successive film transfer process. Experiment results for several multilayer geometries will be compared to numerical and analytical solutions for the buckling wavelength and the resulting calculation of the film modulus.

9:30 AM O9.4
Fiber-Optics Low-Coherence Integrated Metrology for in-situ Non-Contact Characterization of Novel Materials and Structures. Wojciech J. Walecki, Alexander Pravdivtsev, Manuel Santos, Kevin Lai, S. H. Lau and Ann Koo; FSM, San Jose, California.

Low coherence optical interferometry [1] has been proven to be an effective tool for characterization of thin and ultra-thin semiconductor Si and compound wafers [2]. In this paper we extend this method to characterization of strained Si wafers, SOI and other novel structures. The metrology of stress and topography of silicon wafers is a mature field. Available solutions are mainly based on large aperture optical interferometers, laser scanning solutions, and capacitance tools. Free space optical interferometers for 300 mm applications are expensive due to high cost of optics and precision mechanical mounts. Due to large dimensions, and mass they are difficult to integrate for in-situ applications, or with other metrologies. Capacitance method however is not suitable for measuring thickness of semi-insulating and insulating materials, and does not provide insight in the internal structure of layered systems such as SOI. Laser scanning solutions are offering better value than these two earlier mentioned technologies. Laser scanning tools are easier to adapt in integrated environment, and have greater potential for in-situ application. They do suffer however from certain inherent limitations of accuracy inherent to scanning technology. In our paper we propose technique nased on our recently developed dual probe low coherence. We demonstrate that this technology has capability to evaluate both surface topography and thickness of measured layers with reproducibility 50 nm (in laboratory conditions). Typical reproducibility of measured stress is shown in Table 1. Due to small probe size and arbitrary large standoff distance this metrology can be easily integrated in in-situ environments and is fully compatible with other optical metrologies such as thin film reflection spectroscopy, Raman spectroscopy or scatterometry. 1. D. Huang, E. A. Swanson, C. P. Lin, J. S. Schuman, W. G. Stinson, W. Chang, M. R. Hee, T. Flotte, K. Gregory, C. A. Puliafito, J. G. Fujimoto, "Optical coherence tomography," Science 254, 1178-1181 (1991). 2. Wojciech Walecki, Frank Wei, Phuc Van, Kevin Lai, Tim Lee,SH Lau, and Ann Koo, "Interferometric Metrology for Thin and Ultra-Thin Compound Semiconductor Structures Mounted on Insulating Carriers",CS Mantech Conference, May 3-6, 2004, Miami Beach, Florida

SESSION O10: Adhesion and Fracture of Thin Films
Chair: Kazuki Takashima
Thursday Morning, March 31, 2005
Room 2022 (Moscone West)

10:15 AM *O10.1
Quantitative Evaluation of Interface Adhesion Strength in Multilayer Films by Nanoscratch Test. Junichi Koike and Atsuko Sekiguchi; Dept. Materials Science, Tohoku University, Sendai, Japan.

Quantitative evaluation of interface adhesion strength is very important in order to undesrstand the mechanical reliability of nanoscale devices. Among various mechanical testing methods reported to date, nanoindentation and nanoscratch methods can be utilized to measure interface adhesion strength in a nanometer scale. However, the obtained data often scatter in a wide range, making quantitative evaluation difficult. This is due to the fact that these methods have a nanometer spatial resolution and are strongly influenced with anisotropic elastic-plastic behavior of an overlayer above the interface. In the present work, physical processes of these nano-testing methods were investigated with finite element analysis (FEA). The effects of the mechanical anisotropy on the measured adhesion strength were also investigated. Finally, nanoscratch test was actually performed on Cu/Ta(1-x)N(x)/SiO2/Si and the interface adhesion strength was evaluated with the aid of FEA. The FEA results indicated that the nanoscratch test induces a large stress concentration of shear and tensile components at the interface. The size of the stress concentration region was of a few hundred nm, indicating the ability of the nanoscratch test in measuring adhesion strength in a nanometer scale. The stress concentration was due to strain incompatibility of the two layers above and below the interface. The orientation-dependent elasticity and plasticity was found to influence the magnitude of stress concentration via the magnitude of strain incompatibility. The adhesion strength of the Cu/Ta(1-x)N(x)/SiO2/Si could be successfully evaluated by taking the maximum tensile stress as a measure of the interface adhesion strength and by taking into consideration of mechanical anisotropy.

10:45 AM O10.2
Adhesion on Metal-Polymer Interfaces during Uniaxial Plastic Deformation. R. van Tijum[1,2,3], W. P. Vellinga[1,2,3] and J. Th. M. DeHosson[1,2,3]; [1]Applied Physics, University of Groningen, Groningen, Netherlands; [2]Materials Science Centre, Groningen, Netherlands; [3]Netherlands Institute for Metals Research, Delft, Netherlands.

In an increasing number of applications metal-polymer laminates are used as plates and afterwards formed to the final shape. During forming the change in roughness along the interface may cause delamination of the polymer coating. We present a numerical study concentrating on the influence of the roughening a rigid metal substrate on the adhesive energy of the polymer-metal interface. The polymer coating is described by various stages of deformations that mimic the response of Poly Ethylene Terephthalate. For the interface between the metal and the polymer a mixed-mode cohesive zone is used characterized by adhesive energy, working distance, maximum stress and a normal/shear stress ratio. The substrate is a self-affine rough rigid material as characterized by the so-called Hurst exponent, the correlation length and the RMS roughness. We find that the adhesive energy of the interface scales with the RMS roughness divided by the correlation length for a particular Hurst exponent, up to the yield point of the polymer coating. After yielding the polymer starts to soften macroscopically leading to lower stresses. This decrease in the stress level occurs also at the interface, resulting in partial recovery of the adhesive energy at the interface. When the macroscopic hardening starts the recovery of the interface stops and the adhesive energy starts to decrease again. In this paper we will further discuss the influence of relevant model parameters, such as interface parameters, elastic modulus of the polymer and coating thickness.

11:00 AM O10.3
In-situ Observations of Cracks Propagating along Interfaces Between Metals and Thin Polymer Films. W. P. Vellinga[1,2], R. van Tijum[1,2] and J. Th. M. De Hosson[1,2]; [1]Materials Science, Applied Physics, University of Groningen, Groningen, Netherlands; [2]Netherlands Institute of Metals Research, Delft, Netherlands.

Interest in the mechanical properties of polymer-metal laminates is rising since they appear in an ever-increasing number of applications, as diverse as car panels and high-tech displays. The mechanical integrity of the interfaces in such applications is important and mechanical failure is commonly assumed to occur at the interface. In this paper we present in situ observations of the propagation of cracks along polymer-metal interfaces employing the so-called Asymmetric Double Cantilever Beam test. Samples consist of Poly-Ethylene Terephthalate (PET) spin-coated on steel, subsequently glued to a glass support. The crack front is observed through the glass, with optical (birefringence) microscopy. Various image correlation and analysis techniques may be necessary to extract the crack front shape as a function of time and position. The observations show that in general the crack propagation involves mode III components and is inhomogeneous in time as well as in space. Whereas the crack movement is smooth on a macroscopic scale, on a microscopic scale crack movement occurs because parts of the front become unstable and moves forward, so that it is ahead of the mean crack position. Subsequently this disturbance spreads laterally along the front for some distance. Results on PET-glass and PET-glue interfaces indicate that such behavior is in fact quite common, and that in extreme cases the lateral movement associated with a disturbance may span the entire crack front (i.e. the sample width). In such cases the forward movement of a crack front in fact consists entirely of lateral movement of "double kinks" moving along the front. Finally, the correlation of crack front propagation and interface roughness, dictated by the metal substrate will be discussed.

11:15 AM O10.4

Macro Stress Mapping on Thin Film Buckling. Philippe Goudeau[1], Nobumichi Tamura[2], Guillaume Parry[1], Jerome Colin[1], Christophe Coupeau[1] and Howard A. Padmore[2]; [1]LMP, SP2MI, University of Poitiers - CNRS, Futuroscope Chasseneuil, France; [2]ALS, Lawrence Berkeley National Laboratory, Berkeley, California.

The development of thin films for industrial applications is constantly increasing because deposition techniques provide new class of materials which are impossible to obtain with classical elaboration processes. The structure which develops during thin film growth is tightly controlled by the deposition process. Thin films deposited by sputtering technique on non epitaxial substrates are often nanocrystallines which confers to the film very interesting properties. Depending on deposited atom energy, thin films adherent to bulk substrates are generally in a tensile or compressive residual stress state which may affect their physical properties and their life time. In the case of thin films deposited at room temperature by direct ion beam sputtering, biaxial compressive residual stresses in the sample plane and interstitial defects in the unit cell are generally observed. The stress magnitude is often very high (larger than the elastic limit of the same material in the bulk state) and thus spontaneous delamination phenomenon such as 1D wrinkling or 2D buckling may appear for a critical film thickness (relaxation of the stored elastic energy) when extracting the sample out side the deposition chamber. Although a lot of theoretical works have been done to develop mechanical models and calculations (elasticity of thin plates, fracture mechanic, finite element and analytical calculations) with the aim to get a better understanding of driven mechanisms giving rise to this phenomenon, only a few experimental work has been done on this subject to support these theoretical results and nothing concerning local stress/strain measurement mainly because of the small dimension of the buckling (few tenth micrometer). In this work, we use micro beam X-ray diffraction (micro-XRD) available on synchrotron radiation sources as a local probe (spatial) for analysing stress/strain field associated with buckling of gold and tungsten thin films. Spontaneous as well as induced delamination is studied. In addition, the local surface curvature in Silicon wafers due to the presence of He bubbles is also investigated. The X-ray diffraction results are correlated with finite element simulations.

11:30 AM O10.5

Interfacial Properties of Pure-Silica-Zeolite Low-k Thin Films. Lili Hu[1], Zijian Li[2], Yushan Yan[2] and Junlan Wang[1]; [1]Mechanical Engineering, University of California, Riverside, California; [2]Chemical and Environmental Engineering, University of California, Riverside, California.

In order to meet the requirements of next generation IC technology, the semiconductor industry is gradually moving away from well-established Al/SiO2 technology to new Cu/low-k interconnects. Significant effort is being devoted to the development of novel low-k materials. Pure-silica-zeolite thin films have been recently demonstrated to be a promising candidate for low-k applications. A key advantage of zeolite-based low-k materials is the ability to lower k while maintaining higher mechanical strength than other amorphous porous low-k materials. With the rapid development in the synthesis process of different zeolite thin films and the evaluation of their electronic performance, characterizations of the mechanical and interfacial properties have also been brought to demand. During the integration process of low-k films with other semiconducting components, interfacial strength of the low-k material/substrate interface plays an important role in controlling the overall performance and lifetime of the integrated devices. In this work, laser induced thin film spallation technique is used to evaluate the interfacial properties of zeolite low-k thin films on Si substrates synthesized with three different hydrothermal methods. Different from other adhesion measurement techniques, laser-spallation methods load the interface in a remote, non-contact manner using laser-generated stress waves. The quantitative results of interfacial adhesion provide a reliable comparative assessment among different low k thin films and have great significance in the further optimization and applications of low-k zeolite materials.

11:45 AM O10.6

Environmental Effects on Crack Characteristics for OSG Materials. Jeannette M. Jacques, Ting Y. Tsui, Andrew J. McKerrow and Robert Kraft; Silicon Technology Development, Texas Instruments, Inc., Dallas, Texas.

As silicon-based microelectronic devices continue to aggressively scale down in size, traditional BEOL dielectric materials have become obsolete due to their relatively high dielectric constant. For 90 nm node devices, the group of materials known as organosilicate glass (OSG) has emerged as a likely choice for intermetal dielectrics. A potential failure mechanism for this class of low-k dielectric films during the manufacturing process is catastrophic fracture due to channel cracking. The driving force for channel cracking is dependent upon several film properties, including the modulus and residual tensile stress. During fabrication, channel cracks can also form in a time-dependent manner due to exposure to a particular environmental condition. Such mechanisms are commonly known as stress-corrosion or environmentally-assisted cracking. Within this work, the environmental impacts of pressure, ambient, solution pH, temperature, and solvents upon the channel cracking of OSG thin films are concisely characterized. All environmental crack growth rates are compared to samples tested within ambient air. Storage under high vacuum conditions can significantly lower crack propagation rates, while exposure to flowing nitrogen gas induces only a minimal reduction. The crack growth rate experiences little fluctuation as a function of solution pH. However, exposure to aqueous solutions can increase the crack growth rate by three orders of magnitude. The impact of active components within conventional CMP slurries on crack behavior was also investigated. The specific relationships between film thickness, environmental conditions, and the crack growth velocity for OSG materials are addressed at length.

SESSION O11/B7: Joint Session: Fatigue and Stress in Interconnect Metallization

Chairs: Paul Besser and Ralph Spolenak
Thursday Afternoon, March 31, 2005
Room 2004 (Moscone West)

1:30 PM *O11.1/B7.1

Thermal Fatigue in Cu Films. Cynthia A. Volkert[1,2], Reiner Moenig[1,2], Erica Lilleodden[1,2], Young Bae Park[3,2] and Guang Ping Zhang[4,2]; [1]Forschungszentrum Karlsruhe, Karlsruhe, Germany; [2]Max-Planck-Institut fuer Metallforschung, Stuttgart, Germany; [3]Andong National University, Andong, South Korea; [4]Shenyang National Laboratory for Materials Science, Shenyang, China.

Cyclic loading of metals can lead to the formation of damage and to failure even at loads that are well within the elastic range. In fact, the loading conditions present in the thin metal films and small metal structures used in many applications are often severe enough to lead to fatigue failure. In this study, TEM and in-situ SEM observations of thermal fatigue damage in sub-micron thick Cu films have been performed. As the crystal dimensions of the samples are decreased below 1 micron, by decreasing film thickness and grain size, a clear deviation from the characteristic fatigue damage of bulk metals is observed. The changes in dislocation structures, damage morphology, and failure lives are attributed to decreased dislocation motion and increased interface contributions. In particular, in samples with dimensions smaller than 300 nm, the damage morphology provides evidence for some surprising deformation mechanisms, such as twin dissolution and faceted grain growth. The implications of these observations on our fundamental understanding of deformation and on the reliability of small metal structures in microelectronic applications will be discussed.

2:00 PM O11.2/B7.2

TEM-Based Analysis of Defects Induced by AC Thermomechanical versus Microtensile Deformation in Aluminum Thin Films. Roy H. Geiss, Robert R. Keller, David T. Read and Yi-Wen Cheng; Materials Reliability, NIST, Boulder, Colorado.

Thin films of sputtered aluminum were deformed by two distinctly different experimental techniques. One experiment comprised of passing high electrical AC current density, 12.2 MA/cm^2 at 100 Hz, through 800 micron long X 3.3 micron wide and 0.5 micron thick patterned interconnect Al lines deposited on SiO_2/Si substrates. The other consisted of mechanical tensile deformation of a free standing Al line 50 micron long X 5 micron wide and 0.5 micron thick at a strain rate of about 10^{-4}/sec. In the electrical tests approximately 3X10^7 W/cm^2 of energy was deposited at 200 Hz resulting in cyclic Joule heating, which developed a total thermomechanical strain of about 0.3 % per cycle. The mechanical test showed a fracture strain of only 0.5 % but did display ductile chisel point fracture. In both experiments, certain grains exhibited large, greater than 30 degrees, rotation away from an initial <111> orientation toward <001>, based on EBSD measurements. TEM analysis of specimens from both experiments showed an unusually high density of prismatic dislocation loops. In the mechanically-tested samples, a high density of loops was seen in the chisel point fracture zone. While in cross sections of highly deformed regions of the electrical test specimens, very high densities, $>10^{15}/cm^3$, of small, <10nm diameter, prismatic loops were observed. In both cases the presence of a high density of prismatic loops shows that a very high density of vacancies was created in the deformation. On the other hand, in both cases the density of dislocations in the deformed areas was relatively low. These results suggest very high incidence of intersecting dislocations creating jogs and subsequently vacancies before exiting the sample. A discussion of this as well as other possible sources of the high vacancy concentration will be presented.

2:15 PM O11.3/B7.3

Employing Thin Film Failure to Form Templates for Nano-Electronics. Rainer Adelung, Mady Elbahri, Shiva Kuma Rudra, Abhijit Biswas, Sahid Jebril, Rainer Kunz, Sebastian Wille and Michael Scharnberg; Materials Science, CAU Kiel, Kiel, Germany.

Recently, we showed that thin film stress can be used to form well aligned and complex nanowire structures [1]. Within this approach we used stress to introduce cracks in a thin film. Subsequent vacuum deposition of metal leads the formation of a metal layer on the thin film and of metal nanowires in the cracks of the substrate. Removal of the thin film together with the excess metal cover finishes the nanowire fabrication on the substrate. As stress can be intentionally introduced by choosing an appropriate thin film geometry that leads to a stress concentration, the cracks and consequently the nanowires can be well aligned. Meanwhile, we have demonstrated how to form thousands of parallel aligned nanowires, x-and y-junctions or nanowires with macroscopic contacts for sensor applications, simply by applying fracture mechanics in thin films. Christiansen and Gösele called this approach "constructive destruction" in a comment in Nature Materials [2]. This gives a hint how to overcome some problems of the approach, arising from the limits of thin film fracture. A generalization of the fracture approach by being "more destructive" can overcome this limitations. This can be illustrated with an example: It is difficult to form pairs of parallel wires with a nanometer distance of the pair, but a micrometer separation between the individual pairs. Structures like this are useful for many contact applications including sensor arrays or field effect transistors. As well as thin film fracture, thin film delamination can be well controlled by fracture mechanics. Latest experiments show that the combination of both, fracture and delamination, forms an ideal shadow mask for vacuum deposition. Cracks with delaminated sides were used as templates for the deposition of pairs of parallel wires consisting out of different materials with only a few 10nm separation. This was done by first sputtering a metal under an angle of approx. 45° through the delaminated crack, which was used as a shadow mask. A second deposition of another metal is done afterwards under the opposite 45° with respect to the sample normal, having the crack located in the middle between both deposition sources. The angle, the delamination height and the crack width determine here the separation of the nanowire contacts. We present several examples which show how these mechanisms of mechanical failure of thin films can be turned into useful templates for various nanostructures. We will focus here on two standard thin film system, these are wet chemically deposited photo-resist and flash evaporated amorphous carbon. These examples are compared with finite element simulations. Moreover, we show how the delamination cracks can be also used as masks for the removal of material. Down to 20nm wide channels produced by ion beam sputtering are shown. [1] R. Adelung et al., Nature Materials, 3, 375, (2004). [2] S. Christansen and U. Gösele, Nature Materials, 3, 357, (2004).

2:30 PM O11.4/B7.4

Degradation of Fracture and Fatigue Properties of MEMS Structures under Cyclic Loading. Jong-jin Kim and Dongil Kwon; School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

The assessment of mechanical properties and reliability is essential to the development, commercialization and miniaturization of microelectromechanical systems (MEMS). The presence of flexural elements in MEMS applications like gyroscopes, optical switches or micromirrors raises concern about the effects of cyclic loading on material degradation or failure. Designing reliable MEMS devices thus requires knowledge of both the strength of such structural materials as silicon and nickel and also of its degradation with use. However, bulk material properties cannot be used directly for microscale systems because these properties deviate from bulk scaling laws when the characteristic dimensions become small. Thus, testing methods in the microscale range are of critical importance. In this study, the effects of cyclic loading on the fracture and fatigue of MEMS structures were investigated by combining resonance and microtensile methods. Microtensile-compatible resonating structures were designed and fabricated by micromachining that consisted of suspended beams, shuttle, combs and two kinds of electrodes with different areas. After these structures were electrostatically operated at their resonance mode by applying an AC voltage with a function generator, a two-step sacrificial-layer removal process was applied. Then static and dynamic loads much larger than electrostatic forces were applied by piezoelectric-driven microtensile techniques. Both tests were conducted in the same loading mode as the resonance test so as not to change failure mechanism, as is essential in accelerated life or degradation tests. Uniaxial stress-strain measurement results showed that tensile and fracture properties degraded with operation time at the resonance mode. Fatigue properties were measured by applying a pulse wave to a piezoelectric actuator: fatigue tests were conducted and fatigue lifetimes measured at various stress amplitudes. Stress-life (S-N) curves showed that fatigue lifetime and fatigue limit degraded with operation time at resonance mode in the same manner as tensile and fracture properties. These results suggest that fatigue damage accumulated during cyclic loading and increased with operation time. The dependencies of the measured properties on operation time were quantified, and fatigue damage was confirmed by failure analysis. Finally, the fatigue damage accumulation and materials degradation due to cyclic loading were discussed in terms of stress and materials.

2:45 PM O11.5/B7.5

Electrical and Mechanical Reliability of Cu Alloy Thin Film for Future Technology Node. Seol-Min Yi[1], Jeong-Uk An[1], Yong-Hak Huh[2], Young-Bae Park[3] and Young-Chang Joo[1]; [1]School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; [2]Strength Evaluation Group, Korea Research Institute of Standards and Science, Deajeon, South Korea; [3]School of Materials Science & Engineering, Andong National University, Andong-si, Kyungsangbukdo, South Korea.

With miniaturization of advanced integrated circuits fabricated using the Cu damascene process, the higher current density is applied to and the thinner barrier layers are used in the lines therein. The high current density and the thin barrier layer may give rise to significant reliability problems, electromigration and drift of Cu into dielectric, respectively. Use of Cu alloy, as far as there is no significant increase in the electrical resistivity compared to that of pure Cu, has been suggested to address such problems. In this study, Mg and Ru were chosen as the alloying elements. Under oxidization ambient, Mg diffuses to the surface of a Cu(Mg) alloy thin film, on which a self-passivating Mg oxide layer is formed to block Cu drift into dielectric material and to enhance adhesion with a capping layer. Ru, which has the electrical resistivity lower than Ta(N) and negligible solid solubility with Cu, is expected not to increase resistivity of the corresponding Cu alloy. To characterize the effect of alloying elements on barrier performance, time-dependent dielectric breakdown (TDDB) under bias-temperature stress (BTS) tests were conducted using a metal-insulator-semiconductor (MIS) structure. Dependence of such effect on insulating material was also investigated. On the other hand, the effect of alloying elements on resistance to electromigration was quantitatively estimated by measurement of the adhesion between conducting metal and capping layers using the standard four point bending method. Since it is established well that the dominant path of electromigration in the Cu damascene structure is along the surface or interface, i.e. between Cu and a capping material, adhesion may be used as a effective measure to characterize the surface or interface. With the results of the microstructural and compositional analysis, the role of each alloy element in its alloy will be identified and discussed.

3:30 PM *O11.6/B7.6

Effect of Microstructure and Dielectric Materials on Stress-Induced Damages in Damascene Cu/Low-K Interconnects. Young-Chang Joo and Jong-Min Paik; Materials Sci. & Eng., Seoul National University, Seoul, South Korea.

The use of copper and low-k dielectrics led to various reliability concerns which were not issues in the interconnects with aluminum and silicon oxide. For Cu/low-k interconnects, stress-voiding of Cu has been addressed to the main failure mechanism. Damascene Cu interconnects show significant differences in both microstructural and stress behavior compared to those of the Al interconnects patterned using the etching process. Large thermal stresses may build up during the successive thermal cycles due to the differences in the coefficients of thermal expansion (CTE) of the component materials. Other than thermal stresses, considerable amount of growth stress that is originated from grain growth may develop in damascene Cu interconnects as well. Furthermore, use of various low-k materials having lower elastic moduli and higher CTE make stress-related failures even more complicated to understand. In this study, the effect of microstructure and dielectric materials on stress-voiding was investigated using both experimental and theoretical approaches. The grain structure and the stress of damascene Cu lines having the width ranging from 0.1 to 2 μm were analyzed using TEM and x-ray diffraction. The contribution of the growth and thermal stress to the entire stress in the damascene structure were estimated by the finite element analysis (FEA). From this result, we developed a simulator based on FEA to assess the growth and the thermal stresses of a via-line structure. It was found that the stress state of a via-line structure varies dramatically depending not only on their geometries but also on the mechanical properties of dielectric materials. The corresponding failure is explained by the level of stress gradient as well as the stress itself. Also, the stress redistribution and relaxation induced by voiding was studied. Using our simulator and its results, the mechanisms of stress-induced failure in Cu/TEOS and Cu/low-k (having the high and the low CTE, respectively) are identified and discussed.

4:00 PM O11.7/B7.7

Comparison of Line Stress Predictions with Measured Electromigration Failure Times. Rao R. Morusupalli[1], William D. Nix[1], Jamshed R. Patel[1,2] and Arief S. Budiman[1]; [1]Materials Science and Engineering, Stanford University, Stanford, California; [2]Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL), Berkeley, California.

Reliability of todays interconnect lines in microelectronic devices is critical to product lifetime. The metal interconnects are carriers of large current densities and mechanical stresses, which can cause void formation or metal extrusion into the passivation leading to failure. The modeling and simulation of stress evolution caused by electromigration in interconnect lines and vias can provide a means for predicting the time to failure of the device. A tool was developed using MathCAD for simulation of electromigration-induced stress in VLSI interconnect structures using a model of electromigration induced stress. This model solves the equations governing atomic diffusion and stress evolution in one dimension. A numerical solution scheme has been implemented to calculate the atomic fluxes and the evolution of mechanical stress in interconnects. The effects of line geometries and overhangs, material properties and electromigration stress conditions have been included in the simulation. The tool has been used to simulate electromigration-induced stress in pure Cu interconnects and a comparison of line stress predictions with measured electromigration failure times is studied. Two basic limiting cases were studied to place some bounds on the results. For a lower bound estimate of the stress it was assumed that the interface can be treated like a grain boundary in Cu. For an upper bound estimate it was assumed that the interface can be treated like a free surface of Cu. Existing data from experimental samples with known structure geometries and electromigration failure times were used to compare the electromigration failure times with predicted stress build-up in the interconnect lines.

4:15 PM O11.8/B7.8

Stress-Induced Void Formation in Passivated Cu Film during Thermal Cycling and Isothermal Annealing. Dongwen Gan, Bin Li and Paul S. Ho; Laboratory for Interconnect and Packaging, University of Texas at Austin, Austin, Texas.

Stress voiding in Cu metallization is a critical yield and reliability concern. Stress-induced void formation in a passivated electroplating (EP) Cu film was studied during thermal cycling and isothermal annealing with the film stress measured using a bending beam technique. An optic microscope was used for the in-situ observation of the void formation and to determine the void density while SEM was employed to measure the void size and AFM for the topography analysis. In thermal cycling, voids were found to form under tensile stress and close under compressive stress, similar to the void formation observed by T.M.Shaw at al [1] in wide copper lines. The ramping rate, film stress as well as the thermal history were found important factors affecting the void formation in thermal cycling. During isothermal annealing, the void density and void size as functions of annealing temperature, and the void size as a function of time when the film was annealed at 250 degrees were measured. A critical temperature and stress were found for the void formation with the void density being proportional to the film stress, and an activation energy of 0.75eV was deduced for the void growth. Finite element analysis (FEA) models were set up to evaluate the local stress gradients in Cu films due to the mechanical anisotropy of Cu crystal, and that in a void vicinity as a function of void size, which was believed to account for the observed initial fast growth of a void. Mechanisms for the void formation are discussed. 1. T. M. Shaw, L. Gignac, X-H. Liu, R. R. Rosenberg, E. Levine, P. Mclaughlin, P-C. Wang, S. Greco, G. Biery, Stress Voiding in Wide Copper Lines, AIP Conference Proceedings, No612,2002, p.177-83.

4:30 PM O11.9/B7.9

Stress Generation in PECVD SiN Thin Films for Microelectronics Applications. Michael Belyansky[1], Nancy Klymko[1], Anita Madan[1], Anu Mallikarjunan[1], Ying Li[1], Ashima Chakravarti[1], Sadanand Deshpande[1], Anthony Domenicucci[1], Stephen Bedell[1], Edward Adams[1] and Sey-Ping Sun[2]; [1]IBM Microelectronics, Hopewell Junction, New York; [2]Advanced Micro Devices, Hopewell Junction, New York.

Stress generation in silicon is becoming one of the major knobs in boosting performance of the leading edge metal-oxide-semiconductor field effect transistor (MOSFET) technology. Substantial increase in device speed has been achieved by an application of highly stressed silicon nitride liner (SiN) films, which in turn produce an uniaxial stress in Si channel leading to electron and hole mobility enhancement. Thin SiN films (about 50nm) deposited by plasma enhanced chemical vapor deposition (PECVD) have been analyzed by a variety of analytical techniques including Fourier Transform Infrared Spectroscopy (FTIR), X-ray reflectivity (XRR), and Rutherford backscattering (RBS) to collect data on bonding, density and chemical composition respectively. Both tensile and compressive SiN films have been deposited and analyzed. Mechanisms of stress formation in SiN thin films are discussed. It has been found that amount of bonded hydrogen as detected by FTIR is higher for compressive films, and correlates with higher film density as determined by XRR. Both the density and number of interfaces in a film, characterized by XRR, affect the stress. Effect of deposition temperature and other process parameters on stress have been studied. Exposure of SiN films to elevated temperature after deposition lead to increase in tension and degradation in compressive stress. Process parameters, such as post-deposition treatments that result in modification of film structure and magnitude of tensile and compressive stress have been delineated.

SESSION O12: Poster Session: Deformation, Growth and Microstructure in Thin Films

Chairs: Thomas Buchheit, Andrew Minor, Ralph Spolenak and Kazuki Takashima
Thursday Evening, March 31, 2005
8:00 PM
Salons 8-15 (Marriott)

O12.1

Dislocation Sources and their Effect in the Initiation of Plasticity at Shallow Indentation Depths. Suman Vadlakonda and Mirshams Reza; University of North Texas, Denton, Texas.

Nanoindentation experiments bring an appreciable interest in materials behavior at shallow depths of indentations. The discrete Elastic-Plastic responses obtained during indentation at shallower depths are of primary interest in understanding the mechanisms of deformations in operation. Many attempts are being made by both modeling and experimental techniques to understand this discrete responses obtained by nanoindentation experiments. Reasons for exhibition of such behavior still remain unclear. In this paper, an attempt is made to understand the effect of dislocation sources during initiation of plasticity that finally define Elastic-Plastic responses and the ongoing deformation processes. Our attempt here tries to probe the dislocation sources effect on deformation mechanisms at shallower depths where nucleation of dislocations and the phenomenon of plasticity become quite complex. The metals of interest in this research work are nanocrystalline and microcrystalline Nickel, microcrystalline Tungsten, and Iron.

O12.2

The Effect of Microstructural Inhomogeneity on Grain Boundary Diffusion Creep. Dorel Moldovan and Kanishk Rastogi; Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana.

Stress concentration at grain boundaries (GB), a phenomena arising from microstructural inhomogeneity, is an important factor in determining the mechanical properties of polycrystalline materials. In this study we use mesoscopic simulations to investigate characteristics of the deformation mechanism of grain-boundary diffusion creep (Coble creep) in a polycrystalline material. The stress distribution along the grain boundaries in a polycrystalline solid under externally applied stress is determined and the mechanism of how topological inhomogeneities introduce stress concentrations and plastic strain localization is investigated. Microstructures with inhomogeneities of various sizes and distributions are considered and their effect on the interplay between GB diffusion and GB sliding mechanisms is quantified.

O12.3

Theoretical and Numerical Stability Analysis of Multi-Layer Coatings Deposited on Soft Polymer Substrates. Shu Guo, Chris M. Stafford and Martin Y. M. Chiang; Polymer Division, National Institute of Standards and Technoloy, Gaithersburg, Maryland.

Thin films are used widely in technological applications involving coatings, optical reflectors and filters, dielectric stacks, and lithographic resists. Multi-layer coatings are common in these devices for both function and manufacturing considerations. The successful fabrication and reliable operation of structures with micro- or nano-features are strongly contingent on an understanding of their mechanical properties. A novel buckling-based metrology has been reported for measuring Young's modulus of multi-layered thin films, but most solutions in literature consider only single layer systems. Based on the classic laminate theory (CLT), mechanical stability of multi-layer coatings deposited on soft polymer (PDMS) substrates will be investigated and analytical solution will be developed. Numerical analysis using finite element analysis (FEA) will also be conducted to verify analytical solutions and compare to experimental results.

O12.4
Transferred to K13.5

O12.5
Defect Nucleation and Crack Propagation in Thin Films. Daniel Pantuso[1], Boris Voinov[2], Murali Seshadri[1], Sarangapani Sista[1], Sadasivan Shankar[1] and Victor Bashurin[2]; [1]Intel Corporation, Hillsboro, Oregon; [2]Intel Corporation, Sarov, Russian Federation.

The integration of new materials in current and future microprocessors technologies has posed several challenges from the process and manufacturing point of view. One of the most challenging issues is related to mechanical reliability of the interconnect structures in the chip back-end interconnect system. It has become evident in recent years with the introduction of weaker low-k ILD materials and Cu metallization. In order to evaluate interconnect reliability during processing and use conditions, a through understanding of the physical phenomena involved is required. This analysis is complicated due to the complex interactions between multiple materials composing the system. It requires detailed understanding of the manufacturing process, complete characterization of the materials involved in the system and accurate models. In this paper, we focus on the physics of thin film stress, defect formation and crack propagation from a material and fracture mechanics point of view [1]. Our analysis is based on micro-mechanics and crack propagation analysis using multi-scale models. We study the crack behavior in multi-stack thin films. We discuss the implementation of micromechanical models to account for dislocation interactions and variations in dislocation densities leading to changes in hardening behavior and defect formation. Finally, we also discuss issues related to material characterization and identify critical parameters required for detailed modeling analysis. References: 1. M. Koslowsky, A. Cuitino, M. Ortiz, D. Pantuso and S. Shankar. "Micromechanical Modeling for Thermo-Mechanical Reliability of Interconnects". MRS Fall meeting, 2004.

O12.6
Fracture and Deformation of Thermal Oxide Films on Si(100) Using a Femtosecond Pulsed Laser. Joel P. McDonald[1], Vanita Mistry[2], Katherine Ray[2] and Steve Yalisove[3]; [1]Applied Physics, University of Michigan, Ann Arbor, Michigan; [2]College of Engineering, University of Michigan, Ann Abor, Michigan; [3]Materials Science and Engineering, University of Michigan, Ann Abor, Michigan.

Femtosecond pulsed lasers have shown promise as means to machine and modify a variety of materials and structures. Molecular dynamic simulations indicate that femtosecond laser pulses can generate shock waves which propagate with speeds up to five times the speed of sound, yielding pressures on the order of 10$\hat{6}$ Gpa that persist several picoseconds after the arrival the pulse at the material. Under the influence of femtosecond radiation, interesting fracture and deformation phenomena potentially related to such shock waves and pressures have been observed in thin films. In our work with thermally grown oxide films on Si(100), we have observed phenomena in which the surface oxide layer is either completely ejected from the Si(100) surface, or forced up from the Si/SiO2 interface resulting in a deformed, dome like feature. The characteristics of the laser-solid interaction were found to be both film thickness and laser fluence dependent. The observation of these phenomena will be discussed in light of the transient stress present in the oxide layer under femtosecond laser irradiation.

O12.7
Effects of Humidity History of the Tensile Deformation Behaviour in Poly(methyl methacrylate) (PMMA) Films. Chiemi Ishiyama and Yakichi Higo; P & I Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Tensile tests of Poly(methyl methacrylate)(PMMA) films were conducted to clarify the effects of humidity history upon their tensile properties using PMMA films. Prior to testing, thin film specimens with a thickness of 100 μm were kept under various relative humidity(RH) conditions(11, 54 and 98 %RH at 293 K) for 3 days to adjust the sorbed water content to each humidity condition. Tensile tests were first performed under the same humidities as those used for storage before testing. These results show the tensile strength of PMMA films tending to decreasing with increasing humidity. Tensile deformation behaviour is more ductile at 11 and 54%RH although drastically changing to a brittle one at 98 %RH. Secondly, testing was performed under a high humidity condition using specimens, which had been kept at 11%RH prior to testing. After 1 hour of a storage term in 98%RH, the tensile strength of PMMA films decreases although the tensile deformation behaviour remains ductile. The tensile deformation behaviour drastically changes to a brittle mode after a 3 day storage term. Thirdly, data obtained a 11%RH using specimens equilibrated at 98%RH show that tensile strength increases and tensile deformation changes from a brittle to a ductile mode after a 1 hour storage term under low humidity. All results suggest that the tensile strength is decreased by moisture around the specimen surfaces. The tensile strength of PMMA is strongly related to the crazing stress, which usually appears on the surfaces of PMMA. Thus, the moisture around the surfaces makes the crazing stress decrease. On the other hand, the results which shows a brittle manner appear when the tests were performed at high humidity conditions using specimens with high water content. This suggests that the ductile mode must be affected by both absorbed water and the moisture around specimens surfaces. The brittle behaviour of PMMA in high humidity may be caused by the rapid growth of a few crazes. It is considered that the crazing behaviour of the brittle mode may be different from that experiential under the other conditions.

O12.8
Texture Control during Low Energetic Growth of Copper Thin Films. Moneesh Upmanyu and Liang Haiyi; Engineering Division, Materials Science Program, Colorado School of Mines, Golden, Colorado.

We demonstrate control of texture as well as its evolution rate during low energetic growth of copper thin films. EAM-potential based molecular dynamics simulations are performed of copper film growth. Using an initial <111>-<110> bi-textured simulation cell, the control is exercised with respect to three deposition conditions; in-plane strain, deposition rate, and angle of deposition. Our results show that in the unstrained case, the thermodynamically stable <111> texture dominates, as expected. However, out-of-plane strain, low deposition rate and oblique deposition angles can result in stable <110> textures. The texture competition can be explained in terms of surface and bulk energetics and kinetics. In cases where <110> texture dominates, the <111> grain are observed to pinch off from the surface, and in some cases result in dislocated <110> grains. We expect this mechanism to play an important role during texture development in early stage of nanocrystalline film growth.

O12.9
Structural Control of Lithium Fluoride Thin Films. Ozgur G. Yazicigil[1,3], Dena Rafik[2], Vassili Vorontsov[2] and Alexander H. King[1]; [1]School of Materials Engineering, Purdue University, West Lafayette, Indiana; [2]Materials Department, Imperial College, London, United Kingdom; [3]Intel Corporation, Hillsboro, Oregon.

Lithium Fluoride thin films are often used as an "electron photoresist," and they have many other potential uses because of their unique optical and electrical properties. A barrier to their application, however, is the poor understanding of how the film structure is affected by the processing. AFM and TEM were employed to study the structure of LiF films, produced by thermal evaporation. The films were studied as-deposited, and after annealing for 10 minutes and 6 hours at 250°C, which corresponds to 0.46 of the absolute melting temperature. AFM in-plane grain size calculations confirmed the results obtained from dark-field TEM studies. The grain sizes of 30nm thick LiF films grew to 1.5 times the film thickness while the grain sizes of 50nm and 90nm films grew to 0.8 and 0.6 times the film thickness, respectively. The porosity was measured and found to range up to 40% (by volume) for the as-deposited films. It is believed that the pores cause grain growth stagnation, especially for the 50nm and 90nm LiF films. The structures of LiF films deposited at room temperature are similar to the Zone 1 structure proposed by Grovenor et al. [1] for metal films. Reference: [1] Grovenor, C. R. M., Hentzell, H. T. G., and Smith., D. A., "The Development of Grain Structure During Growth of Metallic Films," Acta Metall. Vol 32 (5), pp.73-781, (1984)

O12.10
Role of Stress on the Phase Control and Dielectric Properties of (1-x) $BiFeO_3$−x $Ba_{0.5}Sr_{0.5}TiO_3$ Solid Solution Thin Films. Chin Moo Cho, Hee Bum Hong and Kug Sun Hong; Materials Science and Engineering, Seoul National University, Seoul, South Korea.

Dielectric properties and structure of (1-x) $BiFeO_3$ (BFO)−x

$Ba_{0.5}Sr_{0.5}TiO_3$ (BST) ($x = 0 \sim 1$) solid solution thin films were investigated. All films were prepared at 600°C on (111) oriented $Pt/TiO_2/SiO_2/Si$ substrates by pulsed laser deposition (PLD) technique. Solid solution could be achieved in all composition ranges, evidenced by X-ray diffraction (XRD) and field emission scanning electric microscope (FE-SEM). The intermediate compositions ($0.4 \leq x \leq 0.8$) exhibit a distinct (111) oriented cubic perovskite structure, while rhombohedra symmetry was found in the $x < 0.4$ range. Dielectric constant and tunability of the compositionally graded (1-x) BFO−x BST films within this region ($0.4 \leq x \leq 0.8$) decreased from 1110 to 920 at 1MHz, and increase from 28.34% to 32.42% at 200kV/cm, respectively, while loss tangent remains constant. A systematic decrease in lattice parameter with BST addition reduced stress due to reduction of lattice parameter mismatch between film and the substrate. In that range, the improvement of the dielectric properties without a degradation of loss tangent is attributed to the presence of the stress relaxation, which was quantitatively confirmed by a surface profiler based on Stoney equation.

O12.11

Influence of Precursor Composition on the Chemical Vapor Deposition of MgAl2O4 Oxides. Sanjay Mathur, Hao Shen, Eva Hemmer and Thomas Ruegamer; Leibniz Institute of New Materials, Saarbruecken, Germany.

We are investigating chemistry-based approaches (e.g., Sol-Gel, hydrothermal, chemical vapor deposition) for the transformation of molecular compounds into nanocrystalline phases, which illustrate that predefined reaction chemistry and atomically precise composition of the precursors enforce a control over morphology, composition and particle size, not possible to achieve by conventional methods. A salient example of the influence of precursor chemistry on the material properties was demonstrated for MgAl2O4 thin films deposited using molecular precursors differing in the chemical composition of their organic periphery. For this propose, three Mg-Al alkoxides, [MgAl2(OPri)8], [MgAl2(OBut)8] and [MgAl2(OBut)4H4] were used as single molecular sources in a low pressure chemical vapor deposition process to obtain nanostructured MgAl2O4 films. The choice of ligand tunes the intrinsic precursor properties (physical state, vapor pressure, decomposition temperature etc.) and despite the similar cation ratio (Mg:Al = 1:2), the films obtained from [MgAl2(OPri)8], [MgAl2(OBut)8] and [MgAl2(OBut)4H4] show significant differences in terms of film properties (crystallinity, morphology, microstructure and growth parameters). Thermally stable Mg-Al tert-butoxide with a moderate vapor pressure produces crystalline, dense and adherent MgAl2O4 films with higher value of hardness. The growth rate was low for the isopropoxide compound that is more volatile but suffers from structural instability and a slight tendency of fragmentation in the gas phase that leads to poorly crystalline films indicated in the diminished hardness of the films. The correlation between microstructure and hardness of films obtained by three precursors was established using cross-sectional TEM studies of foils prepared by focussed ion beam (FIB). Our investigations underline that the figure of merit of the precursor is a trade-off between chemical parameters (vapor pressure, structural and thermal stability, nature of ligand, etc.) and the targeted material properties (amorphous or crystalline, dense or porous).

O12.12

Precipitation of Macroscopically Compound-Curved Graphite from Molten Metal. Steven Mason Winder and Jonathan W. Bender; Chemical Engineering, University of South Carolina, Columbia, Columbia, South Carolina.

Kish graphite, a waste product of steel production, is routinely produced by precipitation of carbon from a solution of carbon in metal, usually iron. This catalytic method of synthesis routinely yields highly crystalline graphite at temperatures well below 2000 degrees C. A similar method is now used to produce highly oriented compound-curved graphite-like material. In principle, the surface of a molten catalyst, such as iron, can be used to impose an almost arbitrary shape on graphene precipitated from the catalyst. As a proof of principle, several nearly spherical graphitic shells have been synthesized within a custom-built high vacuum oven by electron irradiation of targets composed of iron (occasionally nickel) and carbon. These shells can be more than 4mm in diameter and hundreds of micrometers thick. Upon cooling, these graphite-like shells routinely exhibit a phase transition in which the initially smooth surface forms striking geometric creases. This phase transition does not appear to coincide with the solidification of the catalyst. The wrinkling phase transition is tentatively identified as an incommensurate-to-commensurate phase transition, in which adjacent graphene layers fall into registry with each other to form locally flat graphite plates with shape and orientation reflecting the crystalline orientation of the material. These facets are bounded by creases–occurring in sets of three–that are frequently resolved under an optical microscope. Ex-situ techniques used to characterize this novel material include SEM, AFM, Raman spectroscopy, and backscatter electron diffraction. The appearance, luminosity, and vapor pressure of the samples is determined during synthesis by CCD camera, light meter, and quartz crystal microbalance (QCM), respectively.

O12.13

Residual Stresses in Anatase-TiO_2 Thin Films Deposited on Glass, Sapphire and Si Substrates. Ibrahim A. Al-Homoudi[1], Linfeng Zhang[2], M. H. Rahman[3], D. G. Georgiev[2], R. Naik[4], V. M. Naik[5], R. J. Baird[2], L. Rimai[2], G. W. Auner[2] and G. Newaz[1]; [1]Mechanical Engineering, Wayne State University, Detroit, Michigan; [2]Electrical and Computer Engineering, Wayne State University, Detroit, Michigan; [3]Chemical Eng. and Materials Science, Wayne State University, Detroit, Michigan; [4]Physics and Astronomy, Wayne State University, Detroit, Michigan; [5]Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan.

Titanium dioxide thin films can be used in many device applications such as gas and humidity sensors, anti-reflection and protective coatings on optical elements, solar energy converters etc. The reliability of any thin film device performance depends, to a large extent, on the residual stresses in the films caused during the fabrication process. Previous studies have shown that the residual compressive stresses may cause film delamination from the substrate whereas the tensile stresses may cause surface cracks in the films [1-3]. The present study deals with the measurement of residual stresses in crystalline TiO_2 (anatase) thin films of different thicknesses (100 to 1000 nm) deposited on glass, sapphire and Si(100) substrates using pulsed D.C. magnetron reactive sputtering. Raman spectroscopy and curvature (deflection) techniques have been used to measure residual stresses in these TiO_2 films. A Ti source in $Ar + O_2$ gas mixture was used at optimized deposition conditions of growth pressure, power, substrate temperature, bias and gas flow to prepare crystalline films of anatase -TiO_2 on 3 different substrates during the same deposition run. By measuring the curvature of substrate before and after the TiO_2 film deposition, the residual stresses were calculated. These results clearly show that the bi-axial stresses are compressive type and decreases with the increase of film thickness. Raman spectroscopy measurements were carried out at room temperature with two different laser excitation wavelengths of 514 and 785 nm to determine the residual stresses in the films at different depths. The dominant E_g mode which occurs at ~ 144 cm^{-1} in single crystal anatase -TiO_2, clearly shifts to a higher value by 2 to 10 cm^{-1} depending on the type of substrate and the thickness of the film. Maximum shift was seen for the films on glass substrate indicating a higher bi-axial compressive stress in agreement with the curvature measurement technique. The excitation wavelength dependent shift of E_g mode clearly shows that the bi-axial stress increases along the film depth, being larger at the film/substrate interface. The correlation between the bi-axial stresses of TiO_2 thin films measured using Raman Spectroscopy and the curvature measurement technique will be discussed. References: [1] C. H. Ma, J.-H. Huang, Haydn Chen, Residual stress measurement in textured thin film by grazing-incidence X-ray diffraction, Thin Solid Films 418 (2002) 73. [2] G. Knuyt, A model for the behavior of tensile and compressive residual stresses developed in thin films produced by ion beam-assisted deposition techniques, Thin Solid Films 467 (2004) 275. [3] Lamartine Meda, Klaus H. Dahmen, Saleh Hayek, Hamid Garmestani; X-ray diffraction residual stress calculation on textured $La_{2/3}Sr_{1/3}MnO_3$ thin film, Journal of Crystal Growth 263 (2004) 185.

O12.14

Nano-scale Material by Design. Deborah A. Bleau[1], Eric T. Eisenbraun[1,2] and Stephen B. Smith[1]; [1]Launcher Technology Division, Benet Laboratories, Watervliet, New York; [2]Albany NanoTech, Albany, New York.

The Future Force of the Army requires products that are smaller, lighter, more portable, with enhanced multi-functionality, increased reliability, reduced power consumption, and lower cost. This research provides the science and technology of enabling atomically engineered nanomaterial for emerging defense applications. These include higher rate of fire cannon technology, future combat systems, and sensor-on-a-chip systems for anti-terrorism and soldier-in-the-field remote sensing and real-time control. Current methods for providing thermal, chemical and erosion protection involve the use of a barrier coating applied to a substrate. This results in discontinuous interfaces between dissimilar materials, which present an abrupt change in material properties and cause low stability bonds due to high energy levels. These higher energy bonds at and near the interface preferentially fail, initiating progressive failure through the protective coatings into the substrate, resulting in ultimate catastrophic failure of the system. Performance of materials will be enhanced by atomically engineering properties with a gradual profile and eliminating the discontinuous interfaces. This research demonstrates innovative techniques for the atomic layer deposition (ALD) of atomically engineered, multifunctional SixCyNz nanomaterials, including the identification of unit and integrated processing concepts for enhanced performance. ALD protocols will be formulated with the ability to tightly control and accurately customize the properties and performance of SixCyNz nanostructural materials. Seed methodologies will be developed that provide the foundation for modeling the atomic scale growth processes and the structural tailoring required to synthesize materials with programmable nanostructure, properties and performance. The modeling correlates the processing parameters with the relative incoming surface flux of Si, C, and N containing constituents and the resulting topographical characteristics of the deposited layers. This provides a first-pass establishment of the efficacy of modeling to link the processing parameters with film characteristics and resulting performance metrics. The impact of altering the flux of reactive species in a plasma CVD environment on the resulting surface coverage characteristics was evaluated and fed back into the process matrix. The results were used to modify the process to yield coatings with enhanced conformality and surface feature irregularity correcting characteristics, which has subsequent bearing on the corrosion resistance and tribological characteristics of the work piece. A continuum-based modeling approach was employed to correlate chemical and structural characteristics of nanoscale coatings with the subsequent thermal and mechanical performance.

O12.15

Influence of Stress on Structural and Dielectric Anomaly of $\mathbf{Bi_2(Zn_{1/3}Ta_{2/3})_2O_7}$ Thin Film. Jun Hong Noh, Hee Bum Hong and Kug Sun Hong; Materials Science and Engineering, Seoul National University, Seoul, South Korea.

Structure, stress, and dielectric properties were evaluated for pyrochlore $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ (BZT) thin films, which were prepared on (111) oriented $Pt/TiO_2/SiO_2/Si$ substrates by pulsed-laser deposition (PLD) technique. Structural analyses such as X-ray diffraction (XRD) and high resolution transmission electron microscope (HR-TEM) indicated that BZT thin film revealed a predominantly (111) oriented cubic pyrochlore structure in contrast to bulk, which is monoclinic. Electron probe microanalysis (EPMA) showed that the composition of BZT thin films was consistent with that of target after deposition. It was found that the compressive stress played an important role to explain the formation of cubic pyrochlore thin film. In cubic thin films, the strain field between grain boundaries was observed by HR-TEM. The position of (444) peak in XRD progressively increase with increasing film thickness, indicating a relaxation of compressive stress in the films, which was also confirmed using a surface profiler based on the Stoney equation. The compressive stress was also reduced due to an appearance of monoclinic phase with decreasing the oxygen partial pressure. It was found that the cubic BZT thin film has a negative temperature coefficient of capacitance (TCC) with - 160 ppm/^{o}C, compared with bulk monoclinic BZT with + 60 ppm/^{o}C. The variances of TCC value approaching zero with decreasing oxygen partial pressure were interpreted by the presence of monoclinic phase, associated with decrease of compressive stress.

O12.16

Improvement of Structural Properties of CdTe/Si for Photonic Applications. Svetlana Neretina[1], N. V. Sochinskii[2] and P. Mascher[1]; [1]Center for Electrophotonic Materials and Devices (CEMD), Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada; [2]Instituto de Microelectronica de Madrid-CNM-CSIC, Madrid, Spain.

CdTe heteroepitaxial growth on Si substrate is a key technology for monolithic integration of HgCdTe/CdTe infrared detector focal plane arrays (FPA) on Si read-out integrated circuits. It has been shown that CdTe epitaxial growth on substrates made from strongly lattice mismatched materials is possible due to the plasticity of CdTe. However, the quality of strained films is generally poor. The effects of rapid thermal annealing (RTA) on CdTe/Si heterostructures have been studied in order to improve the structural quality of CdTe epilayers. Samples of CdTe (111) polycrystalline thin films grown by vapour phase epitaxy (VPF) on Si (100) substrates have been investigated. The strained structures were rapidly thermally annealed at 400°C, 450°C, 500°C, 550°C, and 600°C for 10 seconds. The microstructural properties of the CdTe films were characterized by carrying out scanning electron microscopy (SEM), X-ray diffraction (XRD), and atomic force microscopy (AFM). We have shown that the structural quality of the CdTe epilayers improves drastically with increasing annealing temperature. The optimum annealing temperature resulting in the high film quality has been found to be 500°C. Additionally, we have shown that the surface nucleation characterized by the island size distribution can be correlated with the crystalline quality of the film.

O12.17

Stress Evolution during Solid State Reactions on Silicon. Davy Deduytsche[1], Charlotte Van Bockstael[1], Christophe Detavernier[1], Roland Vanmeirhaeghe[1] and Christian Lavoie[2]; [1]Solid State Physics, University Ghent, Ghent, Belgium; [2]IBM T.J. Watson Research Center, Yorktown Heights, New York.

The growth stress has been investigated during the solid state reaction of different metals with a single crystal Si(100) substrate using substrate curvature measurements. Films of various metals (e.g. Ni, Co, Ti, Pt) were deposited onto thin Si substrates. After deposition, the samples were annealed at a constant heating rate (3°C/s) in a home-built measurement system. In situ wafer curvature and laser light scattering measurements were used to continuously characterize the evolution of stress and roughness of the film during the solid state reaction. The intrinsic stress (or growth stress) produced by the phase formation was investigated and the experimental stress data was analyzed using the model of Zhang and d/Heurle [1]. Changes in wafer curvature are attributed to the growth of different silicide phases. The thermal stress during cooling was used to evaluate the elastic modulus and the mismatch in thermal expansion between film and substrate. [1] S.-L. Zhang, F.M. d/Heurle, Thin solid films, 213 (1992) 34.

O12.18

Residual Stress and Microstructure Properties of Cu/Ta Multilayer Thin Films. Ming-Hsin Cheng[1], T. C. Cheng[1], W. J. Huang[1], C. C. Hsu[1], M. N. Chang[1] and M. K. Chung[2]; [1]National Nano Device Laboratories, Hsinchu, Taiwan; [2]Panalytical, Taipei, Taiwan.

The residual stresses in Cu/Ta multilayer films deposited by DC magnetron sputtering on Si substrate with various annealing temperature were investigated. The residual stresses were determined by X-ray diffraction method with $\sin^2\psi$technique. Consequently, the elastic property (Young$'$s modulus) and hardness in the thin films were performed by nanoindenter for residual stress measurement with X-ray diffraction method because the mechanical behaviors of bulk materials and thin films are different. The results indicated that the tensile stress values in the Cu films using thin films elastic constant for residual stress measurement are higher than those using bulk material elastic constant and the tensile stresses in the Cu films are increasing at higher annealing temperature. Besides, the microstructural properties would be characterized by grazing incidence X-ray diffraction (GIXRD) and X-ray reflectivity (XRR). The XRR spectra were fitted to determine the thickness, density and interfacial roughness in Cu/Ta multilayer structure. Additionally, the effects of microstructure properties and residual stress by scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (TEM) were also observed in this paper.

O12.19

Stress and Grain Size Effects on Epitaxial PZT Thin Films. Oscar Blanco[1] and Jesus Heiras[2]; [1]CIM, Universidad de Guadalajara, Guadalajara, Jal., Mexico; [2]CCMC, Univ. Nacional Autonoma de Mexico, Ensenada, BC, Mexico.

Epitaxial ferroelectric thin films of lead zirconium-titanium oxide, Pb(Zr0.53Ti0.47)O3 (PZT), were successfully grown on SrTiO3 (STO), LaAlO3 (LAO), and Sr(Nb)TiO3 (SNTO) single crystal substrates by a modified rf sputtering technique at high oxygen pressures. The structural properties of the films, evaluated by $\theta/2\theta$, ω and ϕ scans, revealed two crystalline orientation relationships: PZT [001] parallel to [001] of the substrate, and PZT [100] parallel to [100] of the substrate. Films grown on LAO substrates showed a bi-domain crystalline structure with the following orientation relationships: PZT [100] parallel to LAO [001] and PZT [001] parallel to LAO [001]. The calculated reticular values were: a = 4.01 Å and c = 4.10 Å, with a tetragonal deformation ratio of 0.22. This work was focused on the calculus of stresses and grain size coefficients and to the analysis of their contribution on peak broadening in the XRD patterns and their effects upon the ferroelectric behaviour. By the building of Williamson-Hall plots allowed us to it was possible concluded that with the enhancement of the crystalline film properties (better epitaxy and more single crystalline domains) the short range stresses contribution on the peak broadening is decreased. In the other hand, the grain size contribution on the peak broadening was increased with the enhancement of the film crystallinity. Finally, the hysteresis vs. field plots showed the influence of local stresses on the ferroelectric properties, and that the best ferroelectric properties were measured in films with the lowest short range stresses contribution. Authors would like to thank D. Schlom and V. Vaithyanathan (PennState Univ.) for their assistance on four-circle XRD analyses. This work was partially supported by Conacyt proj. 40604-F, DGAPA-UNAM proj. IN116703 and PromeP-UdeG CA-379.

O12.20

Contribution of Internal Strain and Ru-deficiency to Magnetic and Surface Properties of SrRuO3 Thin Films. Young Zo Yoo[1], Omar Chmaissem[1], Alan Genis[2], Gregg Westberg[2], Michael Haji-Sheikh[2], Stanislaw Kolesnik[1], Dennis E. Brown[1], Bogdan Dabrowski[1] and Clyde W. Kimball[1]; [1]Physics Department, Northern Illinois University, Dekalb, Illinois; [2]Electrical Engineering Department, Northern Illinois University, Dekalb, Illinois.

SrRuO3 (SRO), a ferromagnetic metal oxide with high thermal conductivity, crystallizes in a pseudocubic perovskite structure of the GaFeO3 orthorhombic family. Investigation of strain effects on SRO is essential for controlling magnetic property as well as understanding their interrelatedness of the residual strain. Heteroepitaxy is usable for this research because internal strain can be tailored easily by the change of some growth parameters such as working pressure during growth and lattice mismatch between the film and substrate. SrRuO3 thin films were grown on SrTiO3 (100) substrates using the pulsed laser deposition method. In order to exploit the correlation between their properties and strains, the change of internal strain was induced by a wide range of oxygen partial pressures from 0.1 to 300 mTorr during growth. SRO films grown in up to 10 mTorr showed substantial strains exceeding 1% whereas strain became less significant at pressures above 10 mTorr. The island growth was dominant for the highly strained films grown at pressures at or below 10 mTorr, followed by step flow growth mode at 60 mTorr, then reverting back into island growth at 300 mTorr. No ferromagnetic properties was observed for any of the highly strained SRO films, but SRO films exhibiting the step flow growth mode showed high curie temperatures. The correlation between oxygen pressure and film properties is discussed in terms of strain and compositional effects.

O12.21

Failure Analysis of Thermally Shocked NiCr Films on Mn-Ni-Co Spinel Oxide Substrates. Min-Seok Jeon, Jun-Kwang Song, Yong-Nam Kim, Hyun-Gyu Shin and Hee-Soo Lee; Korea Testing Laboratory, Seoul, South Korea.

There has been increasing concerns in thermal shocked failures of coatings for sensor applications in recent years. In addressing ceramic sensor reliability, the understanding of the failure mechanisms is required. Sensor coatings such as NiCr/Mn-Ni-Co-O element experience change of temperature when they are used for non-contact temperature sensor applied to automotive, laser printer or home appliances. It was known that this temperature change induced an error of sensor during its long term operation. In addition, temperature cycling was found to be one of the main factors that create defects in thin coatings due to the large thermal mismatches among coating layers. Therefore the assessment of the durability and characteristics of the layered sensing element are needed by an ADT(accelerated degradation testing) with a thermal cyclic method. Thermal shock was given to NiCr/Mn-Ni-Co-O samples and their characteristics were compared before and after the accelerated degradation testing. This work is focused to analyze failure mechanisms of NiCr/Mn-Ni-Co bi-layer by thermal cycling. The accelerated degradation testing was performed to NiCr/Mn-Ni-Co-O bi-layer in three temperature range of $\Delta T=150$, 175 and 200 °C. The NiCr coatings were considered to have failed when the sheet resistance was changed by 30%. As the cyclic repetition of thermal shock increased, the sheet resistance of NiCr coatings increased. The number of cycles in failure was represented well by a Weibull distribution. The distribution was found to be relatively well behaved with similar shape factor, which suggested that the failure mechanism was the same for the three conditions. The Coffin-Manson equation was applied to the failure mechanism of NiCr coatings. The Coffin-Manson coefficient was turned out to be 3.97, which was consistent with a brittle fracture of hard alloys or intermetallics. Failure mechanism of NiCr films was verified by analyzing the failure sites after thermal cycling by scanning electron microscopy and X-ray photoelectron spectroscopy.

O12.22

Influence of Energetic Particles on the Microstructure and Stress State of Sputtered Thin Films. Aurelien Debelle, Anny Michel, Gregory Abadias and Christiane Jaouen; Laboratoire de Metallurgie Physique, Futuroscope-Chasseneuil Cedex, France.

The control of the microstructure and stress state of thin films are an increasingly important technological issue from a reliability and performance point of view. However, they are process sensitive, and therefore tightly dependent on the deposition conditions, such as pressure, temperature or geometry. Another important factor to consider is the energetic particles involved in the sputtering process, namely the sputtered atoms and backscattered neutrals. The energy and flux of those particles are linked to the target/sputtering gas mass ratio Mt/Mg. Many studies, where this ratio was varied, focused on the respective role of each kind of particles, but until now this is still subject to controversy. The aim of the present study is to separate the influence of the sputtered and backscattered atoms on film microstructure and stress state. Under this perspective, Mo thin films grown on neutral (001) SiO2/Si substrates are elaborated by ion beam sputtering using two different gases, Argon and Xenon. Indeed, in the case of Xenon, the ratio Mt/Mg is such that the quantity of backscattered neutral atoms is negligible. In addition, the epitaxial growth of Mo thin films on (11−20) single-crystal sapphire substrates is investigated. The differences in microstructure (mosaic spread, coherency length, roughness) and stress level in the films grown on Si are investigated by combining X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). The evolution during thermal annealing is also studied. Results show that, as expected, the microstructure and the stress state of the films depend on the sputtering gas. During complementary studies, no significant influence of the thickness, the energy of the sputtering ion beam and the deposition rate was found. Thus, it seems that the fundamental parameter to consider is the total energy deposited on the condensing film, delivered by both particles seamlessly. However, the adhesion of the film on the Si substrate is clearly affected by the trapped gas, as observed during thermal annealing. Concerning the films grown on oriented substrates, an epitaxial growth develops at room temperature but differences exist between films elaborated using Ar or Xe.

O12.23

Cr Films Sputter-Deposited from a Line-Source onto Tilted Substrates. S. Yu. Grachev[1], J.-D. Kamminga[1] and G. C. A. M. Janssen[2]; [1]Netherlands Institute for Metals Research, Delft, Netherlands; [2]Department of Materials Science and Engineering, Delft University of Technology, Delft, Netherlands.

Metal thin films are used in a wide range of applications as protective coatings, conductive layers and for decorative purposes. Sputter-deposition is an effective method to produce metal coatings on industrial scale. The microstructure of a coating is dependent on many parameters and fundamental processes occurring during and after deposition. One of such parameters is angular and energy distribution of the flux, which defines effects of shadowing, re-sputtering and may influence surface diffusion. We report on the microstructure of Cr films produced by sputter-deposition from an elongated target onto substrates tilted around the axis parallel to the target elongation. The flux of the deposited atoms in such a geometry is highly anisotropic, especially at low Ar pressures, due to the target elongation. Also, the tilt of the substrate introduces anisotropy. Cr films were deposited onto 45° tilted substrates at Ar pressures of 1.5x10^{-3} and 6.3x10^{-3} mbar, at temperature 50-100 °C. At lower Ar pressure columns grew straight under tilt angle of 43° with respect to the substrate normal, which is close to the average angle of the arriving flux. This is in contradiction with the "tangent rule", which predicts a tilt of $\sim$26°. At higher pressure the tilt of the columnar microstructure was less, only 28°, which can be explained by the wider, less directional flux from the target. The "tangent rule" is an empirical law for the inclination of a columnar structure produced by a point source. The observed deviation from the tangent rule is attributed to the elongation of the target and the associated it spread of the flux angular distribution in the plane of elongation. The flux itself was mapped with the use of a diaphragm and reflected the elongated geometry of the target.

O12.24

The Effect of Porogen on Physical Properties in MTMS-BTMSE Spin-on Organosilicates. Byung Ro Kim, Jeong-Man Son, Jungwon Kang, Kiyoul Lee, Gwigwon Kang and Minjin Ko; LG Chem, Daejeon, South Korea.

Decreasing the circuit dimensions is driving the need for low-k materials with a lower dielectric constant to reduce RC delay, crosstalk, and power consumption. In case of spin-on organosilicate low-k films, the incorporation of a porogen is regarded as the only foreseeable route to decrease dielectric constant of 2.2 or below by changing a packing density. In this study, MTMS-BTMSE copolymers that had superior mechanical properties than MSSQ were blended with amphiphilic block copolymers used as sacrificial pore generators. While adding up to 40 wt % porogen into MTMS:BTMSE=100:50 matrix, optical, electrical, and mechanical properties were measured and the pore structure was also characterized by PALS. The result confirmed that there existed a tradeoff in attaining the low dielectric constant and desirable mechanical strength, and no more pores than necessary to achieve the dielectric objective should be incorporated. When the dielectric constant was fixed to approximately 2.3 by controlling BTMSE and porogen contents simultaneously, the thermo-mechanical properties of the porous films were also investigated for the comparison purpose. Under the same dielectric constant, the increase in BTMSE and porogen contents led to improvement in modulus measured by nanoindentation but deterioration of adhesion strength obtained by the modified edge lift-off test.

SESSION O13: Characterizing and Understanding Thin Film Growth Stresses

Chair: Junichi Koike
Friday Morning, April 1, 2005
Room 2022 (Moscone West)

8:30 AM *O13.1

The Effects of Atomic and Nano-Scale Processes on Growth Stresses in Thin Films. Carl V. Thompson[1], Cody A. Friesen[1,2], Reiner Moening[1] and Jeffery Leib[1]; [1]Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]Arizona State University, Tempe, Arizona.

Detailed studies of stress evolution during growth and during interruptions of growth of polycrystalline and single crystal Cu and Ag films will be reviewed. Reversible stress changes occur during interruption of all stages of Volmer-Weber growth of polycrystalline films, including the pre-coalescence stage. Reversible stress changes are also observed during interruption of homoepitaxial growth and have been related to changes in the atomic and nano-scale surface structure of the film. While stress changes during growth interruptions are reversible, the subsequent evolution of stress during further film growth can be affected by the growth interruption. This is especially the case in the pre-coalescence stage of Volmer-Weber growth, probably due to island coarsening during growth interruptions. Studies of stress evolution during and after growth interruptions are shown to provide insight into the atomistic and nano-scale mechanisms affecting residual growth stresses.

9:00 AM O13.2

Stress Evolution During Electrodeposition of Ni Thin Films. Sean J. Hearne and Jerrold A. Floro; Sandia National Labs., Albuquerque, New Mexico.

The evolution of stress during electrodeposition of Ni films on gold substrates has been investigated as a function of bath chemistry and deposition conditions to examine the microstructural origins of intrinsic stress from an additive free sulfamate bath. Three likely sources for the rate dependent compressive stress investigated were: interstitial hydrogen / impurity incorporation, capillarity stress, and a chemical potential gradient driven atom incorporation model. Our study definitively proves that the historically important hydrogen incorporation model was not the source of the observed rate-dependent compressive stress. Additionally, we determined that only the chemical potential gradient driven atom incorporation model could not be discounted as the source of the compressive stress. This work was supported by the DOE office of Basic Energy Science. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:15 AM O13.3

”In situ” Nanocomposite Formation in Low-energy Nitrogen Ion Implanted Vanadium-Titanium Alloys. The Role of Sample Temperature on the Microstructure and Tribological Properties. Carmen Ballesteros[1], M. I. Ortiz[2], J. A. Garcia[3], M. Varela[1], J. P. Riviere[4] and R. Rodriguez[3]; [1]Fisica, U. Carlos III de Madrid, Leganes, Madrid, Spain; [2]Tecnologia Electronica, ETSIT- U. Politecnica de Madrid, Madrid, Spain; [3]Centro de Ingenieria Avanzada de Superficies, A.I.N., Cordovilla, Pamplona, Navarra, Spain; [4]Laboratoire de Metallugie Physique, U.Poitiers U.M.R. 6630 CNRS, Futurscope-Chasseneuil, France.

Vanadium-based alloys are promising candidates as structural materials for fusion power devices. The addition of Ti solute results in the improvement of the mechanical properties, increasing their creep resistance and suppressing irradiation swelling. However these alloys show a poor tribological performance(1,2). Active research on low-energy high-fluence ion implantation into metallic targets have been developed in the last years to improve their tribological properties. Low-energy high-temperature nitrogen ion implantation is an intermediate treatment between ion implantation and plasma nitriding, where the ballistic and diffusion processes are combined. A detailed structural and tribological characterization of low-energy, nitrogen implanted V5at. %Ti alloy is presented. Samples were nitrogen-implanted at 1.2 kV and 1 mA/cm2, up to a dose of 1E19 ions/cm2, at temperatures between 400-575 °C. Alloys were analysed by transmission electron microscopy, energy-dispersive x-ray spectroscopy, x-ray diffraction and grazing x-ray diffraction. Depending on the implantation temperature, the ion beam treatment dramatically changes the microstructure of the material. Partial amorphization, nitride precipitation and dislocations are imaged. Tribological properties: microhardness, friction and wear have been improved after low energy N implantation at temperatures above 400°C. The measurements indicate that this improvement increase as the implantation temperature increases. A clear correlation between the microstructure of the implanted layer and the improvement in the tribological and mechanical properties has been demonstrated. TiN precipitation appears to be responsible for the improvement of the tribological properties. For implantation at 575°C a nanocomposite layer is formed at the sample surface where the reinforcement particles are TiN precipitates. Further studies are needed to investigate the effect of the implantation temperature on the microstructure and tribological properties of other metallic alloys. The results indicate that an accurate selection of the implantation temperature determines the tribological performance of the V alloys and the thickness of the layer affected by the implantation. The implantation temperature selects the main process activated by the implantation, ballistic or diffusive. References 1. M. Varela, J.A. García, R.Rodríguez and C. Ballesteros. Nanotech. 2003. 3, 207 (2003) 2. J.A.García, R. Rodríguez, R. Sánchez, R. Martínez, J.P. Rivière, P. Méheust, M. Varela, D. Cáceres, A. Muñoz, I. Vergara, C. Ballesteros. Vacuum 67, 543 (2002). Acknowledgments Authors would like to thank the support received from CICYT through the project MAT-99-1012. TEM work has been made at LABMET, associated to the Red de Laboratorios de la CAM.

9:30 AM O13.4

Chemical and Mechanical Stability of Driven Interfacial Alloys under Ion Irradiation of Mo/Ni Multilayers. Gregory Abadias[1], Christiane Jaouen[1], Franck Martin[1], Jerome Pacaud[1], Philippe Djemia[3] and Francois Ganot[2,3]; [1]Laboratoire de Metallurgie Physique, UMR 6630, Universite de Poitiers, Futuroscope-Chasseneuil, France; [2]Laboratoire des Milieux Desordonnes et Heterogenes, Universite Pierre et Marie Curie, Paris, France; [3]LPMTM, Universite Paris-Nord, Paris, France.

The presence in some metallic superlattices of elastic ”anomalies” (hardening or softening of elastic modulus as compared to that of the bulk counterpart) has been the subject of a much interest. If the role of the interfaces has long been recognized, the underlying physical origin (dilatation or coherency strains, structural disorder, electronic transfer...) remained subject to controversy. Recently, we have shown that the formation of metastable and supersaturated interfacial solid solutions, structurally and mechanically unstable, was responsible for the huge shear elastic softening (-62%) observed in Mo/Ni superlattices with decreasing bilayer period [1]. The present study provides experimental data on phase transformation in ”driven” alloys, by addressing the issue of the stability of alloyed interfaces in Ni/Mo superlattices under ion irradiation. Ni/Mo multilayers with period (Λ)ranging from 0.8 to 87 nm were grown by ion beam sputtering. Ion irradiation was performed at room temperature with 380 keV Ar ions in a large range of fluences to study the influence of stress relaxation and ion-driven interdiffusion on the evolution of the shear elastic modulus. By combining X-ray Diffraction and Brillouin light scattering experiments, we obtained a complete structural and elastic response of the system to ion irradiation. At a very low irradiation dose (0.1 dpa), the relief of the lattice expansion and associated intrinsic compressive stresses occurs with no change in the shear elastic modulus. At higher ion fluences, ion-induced mixing is clearly evidenced from the evolution of the XRD profiles, but an asymmetrical behavior is observed between Mo and Ni sublayers. A strengthening or softening of the shear modulus is observed depending on the period Λ. Thus, irradiation reveals the complex interplay between mixing and elastic properties. Eventually, the mixing process destabilizes the interfaces and leads to the formation of a homogeneous Mo-Ni solid solution. 1. G. Abadias, C. Jaouen, F. Martin, J. Pacaud, Ph. Djemia, F. Ganot Phys. Rev. B 65, 212105 (2002)

9:45 AM O13.5

Nonlinear Transient Finite Element Analysis of the Relaxation Mechanisms in Strained Silicon Grown on SiGe Virtual Substrate. Faouzia Sahtout Karoui, A. Karoui and G. A. Rozgonyi; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina.

To prevent the degradation of electronic properties of strained Si on Si(1-x)Ge(x) virtual substrate, it is necessary to precisely control the stresses during the growth. The stress is originated by the lattice mismatch, differences in thermal-expansion coefficients and incorporated point defects. Si and Ge have a lattice mismatch of $\sim$4%, which causes plastic flow and a high density of misfit and threading dislocations. It is almost impossible to experimentally quantify the plastic strain accumulating in the structure during the growth process. In this case, residual stresses are often calculated from the measured strain, assuming a linear elastic distortion of the crystal lattice. The manufacturing of Si strained/Si(1-x)Ge(x) heterostructure requires a multi-step process. Each of these steps can induce plastic deformation and/or elastic stress relief. Therefore, we investigated in this study, the elastic and plastic strain evolution during deposition using a nonlinear transient finite element analysis. The time and temperature dependent plastic and elastic deformations were considered to account for the relaxation mechanisms. The strain and stress were tackled dynamically at each step level using birth and death of elements. This allowed us to take into account at a given step, the stress history accumulated in the structure during previous steps. We obtained the distribution of the residual stresses and strains throughout the structure for x= 0.2 and x = 0.4, as well as the elastic and plastic contribution to the total misfit strain. Structural parameters were deduced, such as the lattice parameter of the strained Si layer, the degree of relaxation of the SiGe graded layer, the time dependent plasticity evolution during growth as well as the misfit and threading dislocation density. We found that the elastic component of the strain is higher in the strained Si layer, about 0.72% for 20% Ge and 1.2% for 40% Ge, in good agreement with experiments. Relaxation occurs from the middle of the SiGe constant layer up to bulk Si. The contribution to total strain is largely plastic in the graded SiGe layer, Si buffer and Si bulk, while it is mainly elastic in the strained Si layer and part of SiGe constant layer. Plastic deformation is also observed in strained Si and SiGe constant layer. The calculated lattice parameter for the strained Si layer is about of 5.50 A for x = 0.20 and 5.52 A for x = 0.40. The average relaxation factor in the SiGe graded layer is about 90%. Calculated Threading Dislocation (TD) density in the strained Si layer is about 5.8x10$\hat{5}$ cm-2 for x = 0.20 and 2.1x10$\hat{6}$ cm-2 for x= 0.40 in agreement with TD density measured by EBIC. The transient analysis shows that plastic flow occurs sturdily during SiGe graded layer deposition and Si(1-x)Ge(x) constant layer re-growth. No yielding occurs strained Si layer deposition and during the first growth of the Si(1-x)Ge(x) constant layer (before chemical mechanical polishing).

SESSION O14: Thin Film Processing

Chair: Eric Stach
Friday Morning, April 1, 2005
Room 2022 (Moscone West)

10:30 AM O14.1

Hafnium Diboride Nanostructured Hard Coatings from Chemical Vapor Deposition of the Single Source Precursor Hf[BH$_4$]$_4$.

Sreenivas Jayaraman[1,3], Yu Yang[1,3], Abhishek Chatterjee[1,3], Pascal Bellon[1,3], Do Young Kim[2,3], Gregory S. Girolami[2,3] and John R. Abelson[1,3]; [1]Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois; [2]Chemistry, University of Illinois, Urbana, Illinois; [3]Fredrick Seitz Materials Research Laboratory, University of Illinois, Urbana, Illinois.

Hafnium diboride is a refractory material with a melting point of 3250 °C, and belongs to the class of transition metal diborides known for their high electrical and thermal conductivity and their good corrosion resistance. These properties and a bulk hardness of 29 GPa make HfB$_2$ an ideal candidate for hard coatings. We investigate HfB$_2$ thin films deposited by chemical vapor deposition using the single-source precursor Hf[BH$_4$]$_4$. The process yields excellent conformal coverage: on a trench 0.27 μm wide and 1.25 μm deep, the inner coating thickness is everywhere $>$ 50 % of the thickness on the top surface. A minimum deposition temperature of 200 °C allows this material to be deposited onto plastic substrates. Films deposited below 500 °C are X-ray amorphous and yield a very respectable nanoindentation hardness of $\sim$ 20 GPa and an elastic modulus of $\sim$ 300 GPa. The films crystallize at an appreciable rate upon annealing at 900 °C. A short duration anneal produces a fine nanocrystalline microstructure that improves the hardness to $\sim$ 30 GPa. Films deposited at temperatures greater than 600 °C are crystalline and highly textured, with characteristic microstructures that are largely independent of the substrate. We will also report our efforts to develop a nanocomposite material: we add atomic nitrogen from a remote plasma source to obtain ternary Hf-B-N thin films. The addition of nitrogen to the growth flux may nucleate additional phases like BN that force the film to be nanocrystalline. However, the addition of nitrogen slows down the rate at which amorphous films crystallize upon post annealing.

10:45 AM O14.2

Analysis of Residual Stress in CVD Diamond Films Coated on WC-Co and High Speed Steel Cutting Tool Substrates.

Zhenqing Xu[1,2], Ashok Kumar[1,2], Leonid Lev[3] and Michael Lukitsch[3]; [1]Mechanical Engineering, University of South Florida, Tampa, Florida; [2]Nanomaterials and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; [3]General Motors Corporation, Warren, Michigan.

The obstacle that limits the commercialization of the diamond coated cutting tools is associated with the poor adhesion strength of diamond films on the cutting tool substrates like WC-Co and high speed steel due to high residual stress inherent in the film as a result of the CVD process. In our study, we investigated the residual stress in diamond films grown on these substrates as a function of film thickness. The microcrystalline diamond films were synthesized from hydrogen (98.5% vol) and methane (1.5% vol) gas mixture in a low temperature of 650 °C by chemical vapor deposition (CVD) process. We also deposited the nanocrystalline diamond films (NCD) on the cutting tool substrates to investigate the residual stress change due to the morphology change from micrometer to nanometer size. The film thickness, obtained by WYKO optical profilometer and cross section scanning electron micrographs, varied from 2 to 30 μm as the growth time changed. The residual stress was determined by three different methods, peak shift measured by X-Ray Diffractometer and Raman spectroscopy, and the curvature method using Stoney/s equation. The discrepancies in the measured stress data among the three methods are probably caused by the inaccuracies of the elastic moduli used in the calculation equation or the Raman and XRD peak shift due to some factors other than the elastic distortion. The adhesion strength of diamond films to the substrates was then evaluated by Rockwell indentation test to investigate the relationship between residual stress and adhesion strength.

11:00 AM O14.3

Passive Layer Formation at Ferroelectric PbTiO3/Pt Interfaces Studied by EELS.

Lianfeng Fu[1], Sascha Welz[1], Rolf Erni[1], Masaki Kurasawa[3], Paul C. McIntyre[3] and Nigel D. Browning[1,2]; [1]Chemical Engineering and Materials Science, University of California at Davis, Davis, California; [2]National Center for Electron Microscopy, MS 72-150, Lawrence Berkeley National Laboratory, Berkeley, California; [3]Materials Science and Engineering, Stanford University, Stanford, California.

Numerous explanations for fatigue and imprint degradation of ferroelectric perovskites have been proposed; however the mechanisms are still the subject of controversy. Recently, significant attention has focused on the possibility that non-ferroelectric ("passive") layers which separate the ferroelectric crystal from the screening charge on its electrodes may be responsible for such effects. Using electron energy loss spectroscopy (EELS), Z-contrast imaging and energy filtered transmission electron spectroscopy (EFTEM) we identified an interface reaction responsible for formation of such passive layers at the Pt/PbTiO3 interface. The experiments have been performed on a 200kV Schottky field-emission gun FEI Tecnai F20 equipped with a high resolution EEL spectrometer and monochromator system. The ferroelectric films under study consist of a lead titanate (PbTiO3) layer grown epitaxially by metalorganic chemical vapor deposition on a (001)-oriented strontium titanate (SrTiO3) single crystal. A Pt electrode layer was deposited on the PbTiO3 as a top contact. Just prior to Pt deposition, the PbTiO3 surface was cleaned by dilute aqueous HNO3 etching, a procedure that has been found to produce a stoichiometric film surface by photoelectron spectroscopy. Z-contrast imaging of the epitaxially grown, defect free SrTiO3/PbTiO3 interface has been performed. Subsequently, the PbTiO3 appears to be decomposed at the Pt interface and an intermediate film containing nano-scale precipitates can be identified. This region consists of amorphous TiO2 and the crystalline precipitates which are identified using EELS as an intermetallic Pt/Pb phase. EELS across the interfaces confirms the structural changes. The Ti L2,3 edges of PbTiO3 and the intermediate layer differ indicating that decomposition of PbTiO3 has taken place. The intensity of the oxygen K-edge features suggests that the intermediate layer is oxygen deficient relative to the PbTiO3 film. The thickness and electronic structure of this near-interface reaction layer are correlated with changes in ferroelectric behavior as measured in switching current studies after fatigue and imprint treatments.

11:15 AM O14.4

Growth Stress and Alloying Effect in Superlattices: A Comparison between Sputtering and Thermal Evaporation.

Aurelien Debelle, Gregory Abadias, Anny Michel and Christiane Jaouen; Laboratoire de Metallurgie Physique, Futuroscope-Chasseneuil Cedex, France.

The physical properties of many materials when deposited as thin films are different from the bulk ones. In the case of multilayers, the properties of the alternating elements can be combined to obtain materials with very different characteristics. Large anomalies in the elastic properties (deviations from the continuum elasticity) were reported for some bcc/fcc multilayer systems such as Cu/Nb or Mo/Ni. The latter exhibits a drastic softening of the C44 shear elastic modulus attributed to the chemical alloying (mainly Ni in Mo) observed at the interfaces, although the bulk phase-diagrams exhibits almost zero solubility. Thus, the driving force for the formation and the stabilization of this metastable alloy remains to be established. This requires an accurate characterization of the strain/stress state of the films in order to separate chemical from growth stress effects. To address this issue, epitaxial Ni(111)/Mo(110) multilayers were grown on (11$-$20) single-crystal sapphire substrates by two methods, namely ion beam sputtering and thermal evaporation. The first technique is known to produce films having high compressive growth stress due to the highly energetic particles involved in the process, while the latter usually involves low tensile growth stress. In addition, in the present case, the epitaxial relationship generates biaxial stresses, generally referred to as coherency stress, existing in both deposition methods.

The complete strain/stress state of these multilayers was determined by X-ray diffraction using the so−called ŏsin2ψ−method≫ adapted to epitaxial thin films, using the ideal directions method. Ion irradiation induced stress relaxation provides additional data of the stress response of the films[1], as the stress level is modified in a controlled manner. The obtained results show that a triaxial state of stress is required to fully describe the stress state of the Mo sublayers. Differences in the stress states of sputtered and thermal evaporated layers are discussed in terms of deposited energy. Moreover, the presented model provides the true stress-free lattice parameter, solely linked to chemical effects. Interfacial mixing during growth is observed in both cases, which proves that the origin of the interfacial alloying cannot be purely ballistic. [1]: A. Debelle, A. Michel, G. Abadias, C. Jaouen, Appl. Phys. Lett. 84, 24 5034-5036 (2004)

11:30 AM O14.5

Kinematics Analysis and Correlation with Residual Stress of the Ni/Si System on Thin Film in MOS Technology.

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The low resistive NiSi phase is very promising for the reduction of the resistance gate and active zone for advanced cmos technologies. Moreover the control of the stress level in silicon devices is an important issue for transistor performance improvement. In this paper we present for the first time a model enable to extract kinetics parameters of the formation of nickel silicide and the residual stress level. The nickel silicide formation sequence used in this study is a three steps process: -Deposition of Ni and TiN film, followed by a Rapid Thermal Anneal (RTA) for the formation of Ni2Si. -Selective etch remove excess nickel which has not been consumed and TiN. -Second RTA below 450C. The samples investigated are silicide films grown on blanket wafers, on SOI and on polysilicon films deposited on a thin oxide layer for different RTA temperatures. From the measurement of the sheet resistance, the kinetics parameters are extracted. Curvature measurement of wafers at each process step gives the total force in the film. The stress is then deduced thanks to the thickness evaluated formely. A FEM model of phase growth based on the weak coupling problem let us to simulate the stress field in the thin film for each time steps The formation of the Nickel silicide in thin film is sequential: The first phase Ni2Si is formed until there is no Nickel source, then the NiSi phase grows by Nickel diffusion at the two interfaces Ni2Si/NiSi and NiSi/Si. Concerning curvature measurement, some recent in situ characterization studies during silicidation bring information on the formation mechanisms and material properties in the quasi steady state regime. Classically the formation is decomposed in several characteristic trends: During the formation of Ni2Si the force is highly compressive, then during the growth of NiSi the total force is relaxed, and finally after the cooling down to room temperature the residual force is tensile. The originality of this study on that aspect is that we present residual force after selective etch and after the second RTA where mechanical force is partially quenched: -After selective etch, at room temperature, the more the Ni2Si thickness is important, the more the residual force is tensile (contrary to the steady state). Then, the formation of the NiSi phase decreases this tensile force. Impact of TiN layer during RTA1 is also discussed. -After a second RTA, the same for all wafers, the residual force is the same for all wafers whatever the mechanical history is. We present then a model able to simulate the impact of the annealings and the cooling steps on the silicide kinetics formation and the stress level within the layers. For the mechanical behavior of the whole system, we introduce a viscoplasticity model. Several characteristic are reviewed: Fast silicidation formation with fast cooling (RTA), slow silicidation formation with slow cooling (Conduction annealing) and mix program.

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Thermal Stress Relaxation of Plasma Enhanced Chemical Vapour Deposition Silicon Nitride. Pierre Morin, Emmanuel Martinez, Francois Wacquant and Jorge Regolini; ST Microelectronics, Crolles, France.

Silicon nitride is extensively used in VLSI, as hard mask, sidewall spacers or contact etch stop layers. Since the 90nm node, it has also been used as ″stressor″ to improve the transistor performances by generating strain in the Si-channel. Tensile Contact Etch Stop layers and Stress gate Memory Techniques are the most common ″process induced stress″ solutions already published [1]. Among the different nitride process, Plasma Enhanced Chemical Vapour Deposition processes provide low temperature layers that fulfil the Front End Of Line CMOS requirements. Moreover, between the process parameters, plasma power allows to tune the stress, from highly compressive values to highly tensile values. However, these layers can drastically evolve during the subsequent integration thermal budgets and change the final device performance. In our study, we aim to characterize the nitride sensitivity to thermal treatments. To this purpose, we have deposited four PECVD nitride films on silicon wafers with different kind of reactors. We evaluated the initial mechanical stress, layer thickness and hydrogen content by respectivelly curvature measurements, ellipsometry and Fourier Transform InfraRed spectrometry. These nitrides presented as-deposited stress values ranging from compressive to tensile. They were submitted to either high temperature Rapid Thermal Anneal (RTA) at 1100°C or longer thermal treatments at medium temperature, from 700°C to 850°C. We measure the evolution of their properties along the different anneals and compare their behaviour to high temperature thermal nitride. We observed that these somewhat stoechiometric nitrides shifted to more tensile stress around 1100−1200 Mpa when submitted to the RTA, independently of their initial stress values. In the same time, the layers can shrink from zero to 10%. At 700°C 850°C, the evolution was slower, but followed the same trend. Assuming viscoelastic behaviours [2], the kinetic of the stress evolution at these medium temperatures is modelled with Maxwell elements. We observe different features at short and long terms that mean that two exponential components are needed to obtain relevant fit. This dual model at medium temperature is consistent with that obtained with the RTA. At the end, we calculated the thermal activation energies and the correspondent viscosities that were compared to data from literature. As a conclusion, we have obtained a simple model of the thermal stress evolution in nitride that will be used to predict the stress shift in practical CMOS applications and within process simulation. [1] Chien-Hao Chen & al., proceeding of VLSI conference (2004). [2] Peter .I.L. Smeys & al., J. Appl. Phys. 78 (4), 2837 (1995).