

SYMPOSIUM U

Stability of Thin Films and Nanostructures

November 29 - December 3, 2004

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* Invited paper

8:30 AM *U1.1/JJ1.1/KK1.1

Kinetic Critical Thickness for Quantum Dot Formation. Yuhai Tu and Jerry Tersoff, IBM Watson Center, Yorktown Heights, New York.

In heteroepitaxial growth of strained layers, the growing layer often remains planar up to some "critical thickness", at which point three-dimensional (3D) islands form. This Stranski-Krastanov transition is of great practical importance. Many device structures require smooth planar layers, while conversely, 3D islands hold promise as self-assembled quantum dots. The transition from planar growth to islands poses a longstanding puzzle in the understanding of heteroepitaxy. As the misfit strain is reduced (by varying the deposited alloy composition), the "critical thickness" is observed to increase dramatically. Transition thicknesses as large as 10-30 atomic layers are seen for InGaAs on GaAs (001), and similar behavior is seen for GeSi on Si (001). We have simulated such strained-layer growth, using a continuum model that consistently accounts for the alloy compositional degrees of freedom. Under generic assumptions, we find behavior closely resembling that seen experimentally. The surface remains flat up to some thickness at which islands suddenly form. This apparent critical thickness depends sensitively on composition, but only weakly on deposition rate. Our results confirm the insightful proposal of Cullis et al., that the key factor controlling the transition is the continuous increase of surface composition due to intermixing during growth. However, the specific kinetic mechanism is unanticipated and surprisingly simple.

9:00 AM *U1.2/JJ1.2/KK1.2

Microscopic View of InAs Quantum Dot Growth and Overgrowth. Klaus Kern, Nanoscale Science Department, Max Planck Institute for Solid State Research, Stuttgart, Germany.

Surfaces and interfaces not only determine to a large extent the properties of small-scale materials due to their high surface-to-volume ratio, they are also an ideal platform for the design, fabrication and device integration of nanostructures. Both top-down and bottom-up methods have been developed for the handling of matter at the molecular and atomic scale. The prime example for the bottom-up fabrication of nanostructures is the Stranski-Krastanov growth of semiconductor quantum dots (QD's), with the model systems Ge/Si(100) and InAs/GaAs(100). Although the self-organized growth of these nanostructures has been intensely studied for more than a decade and a number of important achievements have been obtained concerning their electronic and optical properties, a definite and coherent picture of the growth scenario is still missing. In this talk I will present a microscopic view of the growth and overgrowth of InAs quantum dots on GaAs(100) obtained by scanning tunneling microscopy. The atomic-scale experiments demonstrate that the shape and composition of the quantum dots are determined by the delicate interplay between thermodynamic and kinetic effects. Moreover, the STM measurements reveal that only two well-defined island shapes, pyramids and domes exist. Both structures are very similar to the island shapes observed in the Ge/Si system suggesting that pyramids and domes are universal island shapes, independent of specific material parameters. Also the overgrowth scenario that emerges from our measurements, in which the QD capping can be described as a backward transition from steeper domes to shallower pyramids, is material independent as long as the surface energy of the cap material is higher than that of the island material.

9:30 AM *U1.3/JJ1.3/KK1.3

Pattern Formation on Silicon and Silicon-on-Insulator.

Max G. Lagally, Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

The strain driven self-assembly of faceted Ge nanocrystals during epitaxy on Si(001) to form quantum dots (QDs) is by now well known. [1] We have also recently provided an understanding of the thermodynamic driving force for directed assembly of QDs on bulk Si (extendable to other QD systems) based on local chemical potential and curvature of the surface. [2] Silicon-on-insulator (SOI) produces unique new phenomena. The essential thermodynamic instability of the very thin crystalline layer (called the template layer) resting on an oxide can cause this layer, under appropriate conditions, to dewet, agglomerate, and self-organize into an array of Si nanocrystals. Using LEEM, we observe this process and, with the help of first-principles total-energy calculations, we provide a quantitative understanding of this pattern formation [3] and show how addition of Ge affects the energies and hence the pattern. The Si nanocrystal pattern formation can be controlled by lithographic patterning of the SOI prior to the dewetting process. The resulting patterns of electrically isolated Si

nanocrystals can in turn be used as a template for growth of nanostructures, such as carbon nanotubes. [4] We show that this growth is controlled by the flow dynamics, and possibly by electrostatics. Growth of heteroepitaxial films on SOI brings with it unique defect generation mechanisms, associated with the Si-oxide interface, that may, in fact, result in the elimination of patterns found for growth on bulk Si. We fabricate thin membranes and free-standing structures to investigate the effect of added uniaxial stress on adatom diffusion and the nucleation and coarsening of 2D and 3D structures on this surface. Finally, nanopattern formation on Si using etching techniques results in unexpected wetting behavior. Aspects of the work were supported by DOE and by NSF. In conjunction with B. Yang, F. Liu, P. Rugheimer, D. Savage, M. Roberts, P. Zhang, V. Joshkin, M. Marcus, and M. Eriksson. 1. Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Letters **65**, 1020 (1990). 2. B. Yang, F. Liu, and M. G. Lagally, Phys. Rev. Letters **92**, 025502-1 (2004). 3. Bin Yang, Pengpeng Zhang, M.G. Lagally, Guang-Hong Lu, Minghuang Huang, and Feng Liu, submitted to PRL. 4. B. Yang, M.S. Marcus, H. F. Tang, P.P. Zhang, Z.W. Li, B.J. Larson, D.E. Savage, J.M. Simmons, O. M. Castellini, M.A. Eriksson, and M.G. Lagally, submitted to Appl. Phys. Letters.

10:30 AM U1.4/JJ1.4/KK1.4

KMC Computations of Strained Heteroepitaxy in 3

Dimensions. Peter Smerka¹, Giovanni Russo², Leonard Sander¹ and Jason Devita¹, ¹University of Michigan, Ann Arbor, Michigan; ²University of Catania, Catania, Italy.

We study the evolution of strained heteroepitaxial films in 3 dimensions using an atomistic model due to Orr, Kessler, Snyder and Sander. This model consists of a SOS type model with nearest and next nearest neighbor bonds. The elastic effects are considered using a ball and spring model with nearest and next nearest neighbor bonds. The strain field in the substrate was deduced using an exact solution which can be efficiently evaluated using Fast Fourier Transforms. Our results show that when the elastic effects are small the films grows in a layer-by-layer fashion. However, when the elastic effects become strong we observe either mound formation or trench type structures depending on the deposition rate.

10:45 AM U1.5/JJ1.5/KK1.5

The Effect of Inhomogeneous Diffusion on the Formation of Quantum Dots. Christian Ratsch, Raffaello Vardavas, Xiaobin Niu and Russel Caflisch; Mathematics, UCLA, Los Angeles, California.

The simulation of the formation and self-organization of quantum dots is a major goal in modeling efforts of epitaxial growth. An anisotropic, spatially varying diffusion constant can lead to preferred island nucleation in certain regions. Such an anisotropic, inhomogeneous diffusion field can be achieved, for example, by burying defects (or other structures) underneath the surface: the inhomogeneous strain field leads to an inhomogeneous potential energy surface, and thus to an inhomogeneous diffusion field. We will show that under the right conditions, nucleation occurs preferentially along certain geometric lines, with all islands being approximately the same size. In addition, there are large denuded zones on the surface without any islands in it. Our results were obtained with an island dynamics model that employs the level-set technique. This approach is particularly well suited for this problem, as both, a spatially varying diffusion field, as well as microscopic events on vastly different time-scales can easily be implemented in our model, without extra computational cost.

11:00 AM U1.6/JJ1.6/KK1.6

On the mechanisms guiding epitaxial island assembly on topographically patterned substrates. Robert V. Kukta, Mechanical Engineering, Stony Brook University, Stony Brook, New York.

A method of self-assembling quantum dot domains that promises substantial flexibility and control is strained layer growth on topographically patterned substrates. Prior to growth, features are introduced on the substrate by a method such as lithography and ion-etching. These features guide morphological development by providing preferred sites for islands to nucleate and grow. While it is known from experiment that the arrangement of islands on patterned substrates is affected both by energetic and kinetic phenomena, the nature of these effects has not been well characterized. There have been few analytical efforts to understand where islands form and why and how they develop at particular sites. It is the purpose of this paper to offer some new insight. A continuum-level model is used where the free energy of system is assumed to consist of surface free energy and strain energy. Energetics is first addressed to understand which sites are most favorable for islands, depending on factors as substrate shape, lattice mismatch between the film and substrate materials, surface energy, and the amount of material deposited. The result is presented in a simple phase diagram. Then the kinetic process of deposition combined with morphological evolution by surface diffusion is simulated. It is found that configurations may arise

that appear to be neither stable nor metastable according to a simple energetic analysis; free energy is reduced as islands translate in certain directions. Yet even with a lengthy post-deposition anneal these configurations do not evolve kinetically. Such configurations are found to represent a novel metastable state wherein islands are locked in energetically unfavored sites because the kinetically pathway admitted by surface diffusion requires evolution through states of higher free energy. It is demonstrated that a critical island size exists for this metastability to occur. Small islands tend to be mobile and able to move to minimum-energy sites, whereas large islands tend to be immobile. This phenomenon results in islands affixed to the side walls of substrate surface features. Focus is limited to growth on small amplitude sinusoidal substrate features as studied in detail recently in a series of experiments by Zhong et al. [J. Appl. Phys. 93, 6258 (2003); Appl. Phys. Lett. 82, 445 (2003)]. Their experiments provide evidence of the novel metastability and also illustrate that both kinetics and energetics have a role in guiding the positioning of islands. Insight to the nature of these effects is obtained from kinetic simulations based on their experiments.

11:15 AM U1.7/JJ1.7/KK1.7

In-Situ Studies of Cu₂O Nano-Island Formation on Cu (001). Jeffrey A. Eastman, Paul H. Fuoss, Guangwen Zhou, Lynn E. Rehn, Peter M. Baldo, Loren J. Thompson and Dillon D. Fong; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

The early-stage oxidation behavior of the Cu (001) surface is being investigated at the Advanced Photon Source via in-situ x-ray diffraction techniques. Single crystal (001) Cu thin films grown on (001) SrTiO₃ substrates are oxidized to form crystallographically-aligned Cu₂O nano-islands on the Cu surface. By measuring oxide island growth kinetics as a function of oxygen partial pressure, the thermodynamic limit between oxide growth and reduction has been determined for several temperatures and film thicknesses. We find the Cu/Cu₂O phase boundary at much larger oxygen partial pressure than predicted by bulk phase equilibria, and also find that the temperature dependence of this phase boundary is smaller than expected. Large reversible changes in the oxide lattice parameter of up to 0.5% in response to controlled variations in oxygen partial pressure in the chamber are also observed, possibly indicating an unexpectedly large stoichiometric range in Cu₂O nano-islands compared with bulk Cu₂O. Significant differences are seen in the oxidation behavior of thin film and bulk single crystal samples, leading to the conclusion that substrate constraints are influencing behavior. The prospects for engineering these constraints to influence nanopattern formation will be discussed.

11:30 AM U1.8/JJ1.8/KK1.8

Orientation dependence behavior of self-assembled (In,Ga)As quantum structures on GaAs substrates. Shahram Seydmohamadi, Zhiming M. Wang, Hong Wen and Gregory J. Salamo; Physics, University of Arkansas, Fayetteville, Arkansas.

The orientation of the substrate can play an important role in the formation of (In,Ga)As quantum structures grown on GaAs. In particular, the unique surface morphology of a high index substrate allows the substrate to act as a template for the growth of self assembled quantum wires (QWRs) and quantum dots (QDs). In this work, the formation of self assembled (In,Ga)As quantum structures are discussed as a function of crystallographic orientation of the GaAs substrates. We report on the effect of the orientation of a GaAs substrate on the evolution of strained (In,Ga)As quantum structures, along one side of the stereographic triangle from (100) towards (111)A, including (100) and (N11)A surfaces, where N is equal to 7, 5, 4 and 3. The samples were grown by UHV molecular beam epitaxy (MBE) and characterized by atomic force microscopy (AFM) and scanning tunneling microscopy (STM). For the same coverage of (In,Ga)As, a transition from zero dimensional (In,Ga)As QDs to one dimensional QWRs is observed as a function of the orientation of the substrate moving from (100) toward (311)A along the stereographic map. While (In,Ga)As QDs form on GaAs (100) and (711)A surfaces, we observe QWRs formation on GaAs (311)A and (411)A surfaces. In between, GaAs (511)A is covered by elongated (In,Ga)As QDs. When taken together with the observation of QDs on the GaAs (100) and (711)A surfaces and QWRs on the GaAs (311)A and (411)A surfaces, the texture observed on the GaAs (511)A surface is interpreted as observing a transition taking place from quantum dots to quantum wires on the (511)A surface. The overview picture then, is that a continuous transition from QD to QWR takes place along the mentioned stereographic direction. We will present an explanation for the transition from QD to QWR behavior along the stereographic triangle based on the changing surface morphology of the substrates.

11:45 AM U1.9/JJ1.9/KK1.9

Energetics of Trench Formation Around Ge/Si Quantum Dots. Dhananjay Tulsiram Tambe and Vivek B. Shenoy; Solid

Mechanics, Brown University, Providence, Rhode Island.

At high growth temperatures, the misfit strain at the boundary of a Ge quantum dot on Si(001) is relieved by the formation of a trench around the base of the island. The depth of the trench has been observed to saturate at a level that depends on the base-width of the island. Using finite element simulations, we show that the self-limiting nature of trench depth is due to a competition between the elastic relaxation energy gained by the formation of the trench and the surface energy cost for creating the trench. Our simulations predict a linear increase of the trench depth with the island radius, in quantitative agreement with recent experimental observations.

SESSION U2/JJ2/KK2: Joint Session: Patterning and Steps on Surface
Chairs: Jim Evans and Vivek Shenoy
Monday Afternoon, November 29, 2004
Room 210 (Hynes)

1:30 PM *U2.1/JJ2.1/KK2.1

One-dimensional interfaces in Two-dimensional Materials Structures*. Ellen D. Williams^{1,2}, Daniel Dougherty², Chenggang Tao², Oleksander Bondarchuk^{1,2}, Theodore L. Einstein^{1,2}, Michael S. Fuhrer² and Philip J. Rous³; ¹MRSEC, University of Maryland, College Park, Maryland; ²Physics, University of Maryland, College Park, Maryland; ³Physics, University of Maryland Baltimore County, Baltimore, Maryland.

Steps, island edges and domain boundaries are one-dimensional interfaces that serve as the locus of material transport, and as interfacial barriers for electron transport. These interfaces fluctuate under thermal excitation, with length and time scales that can be observed directly using scanning probe imaging. Quantitative characterization of these fluctuations using the tools of statistical mechanics yields energetic and kinetic parameters that can be used to predict evolution of structure under external driving forces (e.g. temperature gradient, growth or sublimation, electromigration). In addition, as the size of the bounded structure decreases into the nanoscale, the stochastic aspects of the fluctuations themselves become a significant component of the material properties. Scanned probe measurement of fluctuations, correlation, autocorrelation, survival and persistence, will be presented for steps (on Ag, Pb and C₆₀/Ag) and domain boundaries (Pb/Si, Ag/Si and C₆₀/Ag). The meaning of system size in designing, evaluating and using these results will be explained. The impact of the one-dimensional structures on electron flow will also be presented. Direct measurements of step fluctuations in the presence of an electromigration current density of up to 10⁵ A/cm² will be shown and interpreted in terms of the limits on effective charge for mass displacement at the line boundary. Measurements of the noise and resistivity in electron transport will be shown and characterized in terms of structural fluctuations in a film near the percolation threshold. * Different aspects of this work have been supported respectively by the DOE-BES, NSF-NIRT and NSF-MRSEC

2:00 PM *U2.2/JJ2.2/KK2.2

A Model of Patterning Molecular Dipoles on Solid Surfaces. Zhigang Suo, Harvard University, Cambridge, Massachusetts.

Abstract Adsorbed on a solid surface, a molecule can migrate and carry an electric dipole moment. A nonuniform electric field can direct the motion of the molecule. A collection of the same molecules may aggregate into a monolayer island on the solid surface. Place such molecules on a dielectric substrate surface, beneath which an array of electrodes is buried. By varying the voltages of the electrodes individually, it is possible to program molecular patterning, direct an island to move in a desired trajectory, or merge several islands into a larger one. The dexterity may lead to new technologies, such as reconfigurable molecular patterning and programmable molecular cars. This paper develops a phase field model to simulate the molecular motion and patterning under the combined actions of dipole moments, intermolecular forces, entropy, and electrodes. Slides of this talk will be available at www.deas.harvard.edu/suo Z. Suo and W. Hong, PNAS 101, 7874 (2004). Y.F. Gao and Z. Suo, J. Appl. Phys. 93, 4276 (2003). W. Lu and Z. Suo, J. Mech. Phys. Solids, 49, 1937 (2001).

2:30 PM *U2.3/JJ2.3/KK2.3

The Quasicontinuum Monte Carlo method for simulating surface growth. Leonard M. Sander¹, Jason Devita¹ and Peter Smereka²; ¹Physics, University of Michigan, Ann Arbor, Michigan; ²Mathematics, University of Michigan, Ann Arbor, Michigan.

We have developed an algorithm for treating growth on surfaces which treats the adatoms as a continuous fluid, and the islands and steps as

collections of discrete particles. The method gives an accurate account of shot-noise fluctuations by converting adatoms to solid one atom at a time. For the case of irreversible growth we can treat fractal island shapes, multilayer growth, the effect of Ehrlich-Schwoebel barriers, and nucleation. The algorithm can, in favorable cases, be faster than Kinetic Monte Carlo. For growth near equilibrium we need to treat attachment and detachment from the islands on the same footing. This is much more delicate than the irreversible case. We will discuss the issues that arise, and how we deal with them.

3:30 PM U2.4/JJ2.4/KK2.4

Continuum Theory of Interacting Steps on Crystal Surfaces in (2+1) Dimensions. Dionisio Margetis¹ and Robert V. Kohn²;

¹Mathematics, M.I.T., Cambridge, Massachusetts; ²Courant Institute of Mathematical Sciences, New York University, New York, New York.

The difference-differential equations of step motion on crystalline surfaces below the roughening transition temperature are formulated for closed interacting steps of reasonably arbitrary shape in (2+1) dimensions. Among the major kinetic processes considered are the diffusion of adatoms across terraces, and the attachment and detachment of atoms at the step edges, with inclusion of the Ehrlich-Schwoebel barrier. Basic ingredients of the formulation are (i) the approximate solution of the Laplace equation for the adatom concentration on each terrace within the quasistatic approach via separation of the space variables into "fast" and "slow" ones and application of asymptotics, and (ii) an analytical expression for the step chemical potential for a sufficiently wide class of step interactions, which include local elastic dipole-dipole interactions as a special case. The continuum limit of the discrete step-flow equations is examined in detail, with particular emphasis on the case with next-neighbor interactions. This limit yields a nonlinear partial differential equation (PDE) of fourth order for the height profile, which accounts for both step stiffness and step-step interaction energy. The PDE is compared to the one derived from the standard surface-free energy considerations and is shown to reduce to the latter under certain local conditions on the step interactions. The role of longitudinal currents, which are parallel to the steps, is discussed.

3:45 PM U2.5/JJ2.5/KK2.5

Formation of Ridges on Patterned Mesas and Their Role in Evolution of Step Arrays on Mesas. Kee-Chul Chang and Jack M. Blakely; Materials Science & Eng, Cornell University, Ithaca, New York.

Mesa structures fabricated on Si(111) surfaces have been experimentally found to develop step arrays with large spacing of the order of a micron or more after annealing at temperatures where sublimation becomes important. These are caused by transient ridges around the edges that initially develop during annealing and form a barrier to step motion before eventually breaking down. This produces a step distribution that can be approximated as an array of steps of the same sign with a few wide terraces. The analysis of the evolution of such an array of steps presents new aspects from those associated with cases where the step train consists of nearly evenly spaced steps. We have done computer simulations using one dimensional Burton, Cabrera and Frank (BCF) theory with attachment-detachment and step-step repulsion for this configuration. The results suggest that under conditions where there is significant motion of the entire train of steps due to evaporation, the widely spaced terraces will persist for a long time. If we include a significant Ehrlich-Schwoebel effect, where the incorporation rate for adatoms from the lower terrace is higher than that for the upper terrace, the steps redistribute to form step density waves that become stable after a short time. With no Ehrlich-Schwoebel effect the steps tend to become uniformly spaced. The predicted distributions will be compared with the experimentally measured ones.

4:00 PM U2.6/JJ2.6/KK2.6

Self-ordering of Nanofacets on Vicinal SiC(0001) Surfaces and Its Application to Heterogeneous Nanostructures.

Satoru Tanaka, Kazunori Terada, Tomoyuki Miyamoto, Masahiro Fujii and Ikuo Suemune; RIES, Hokkaido Univ., Sapporo, Japan.

Surface nanostructures by taking advantages of self-ordering or self-organization have been attracted much attention in nanofabrication of semiconductor device structures. Periodically and spontaneously ordered semiconductor surfaces reveal significantly fine and spatially uniform patterns, which are beyond the lowest limit of electron beam lithography. Formation of step/terrace structures is typically observed on vicinal surfaces. Technologically important substrates such as Si and GaAs have been studied, both for device applications and for understanding of basic surface physics. Silicon carbide is an important compound semiconductor, which possesses polymorphism and a variety of superior characteristics such as wide band-gap and significantly electronic properties. It is thus a promising

semiconductor for the next generation of high power and high frequency electronic devices. Initially, we have investigated step/terrace configurations appeared on vicinal SiC(0001) surfaces after high temperature H₂ annealing and found that self-ordered nanofacets, consisting of pairs of (0001) and (11-2n), were generated [1]. The origins of such periodic nanofacets were discussed in terms of equilibrium surface phase separation and surface elasticity theory followed by Marchenko et al.[2]. Note here that the periodicity of such nanofacets on 4H and 6H-SiC surfaces is superior to other materials such as Si and GaAs. We believe this is due to its polytypic nature. In this presentation we report such ordered nanofacet formation under various etching conditions and discuss possible control of surface nanostructures and also show an application to heterogeneous epitaxial system such as GaN nucleation on SiC. [1] H. Nakagawa, S. Tanaka, I. Suemune, Phys. Rev. Lett. 91, 226107-1(2003) [2] V. I. Marchenko and A. Y. Parshin, Sov. Phys. JETP 52, 1 (1980).

4:15 PM U2.7/JJ2.7/KK2.7

The Controlled Self-Assembly of Nano-Structures by the Activated Stranski-Krastanow Transition Method. Cheng-hsin Chiu, Z. Huang and C. T. Poh; Department of Materials Science, National University of Singapore, Singapore, Singapore.

The growth of nano-crystalline islands on the surface of Stranski-Krastanow (SK) film-substrate systems by self-assembly is a promising technique for device applications. A critical issue in realizing the self-assembly technology is to control the sizes, the locations, and the shapes of the nano-structures. In this talk we propose that the controlled self-assembly of nano-islands can be achieved by a novel scheme, namely the activated Stranski-Krastanow transition (ASKT) method. The basic idea of the ASKT method is to make simple patterns on a flat surface of the SK system in a special thickness range and then anneal the system to activate the self-assembly of the patterns into islands. The method can control the island locations, and by varying the geometry of the patterns, the method has the capability to produce different island structures. For example, changing the size, the aspect ratio, and the height of a rectangular pattern, the ASKT method can yield a two-by-two island array, a square ring with a single or multiple rims, and multiple wires. In addition, the feature length of the structures can be a small fraction of the pattern size, and the length can be tailored by adjusting the mismatch strain in the film without reducing the pattern size. Most importantly, the instability of the nano-structures against coarsening and shape transition, a common phenomenon that causes serious problems in device applications, can be avoided in the ASKT method. The theory of the ASKT method is presented in this talk together with three-dimensional numerical simulation that demonstrates the potential capability of the ASKT method.

4:30 PM U2.8/JJ2.8/KK2.8

Stability and Evolution of Nano-ripples on Crystalline Surfaces. Ashwin Ramasubramanian and Vivek B. Shenoy; Division of Engineering, Brown University, Providence, Rhode Island.

The relaxation of nano-ripples on metallic and semiconductor surfaces is studied using a nonlinear continuum approach that accounts for the formation and interaction energies of surface steps as well as the Schwoebel barrier at step-edges. This method is used to model recent experimental studies of relaxation of a Cu(001) surface. The relaxation process is in the attachment-detachment kinetic regime at the temperatures of interest here. Ripples are seen to decay with the formation of step-free regions or facets which indicates that the line-tension of the steps plays an important role in the decay behavior. Although the ripples have a dominant spatial frequency or wavelength, our studies find that the decay behavior is not same as that of a sinusoid of a single wavelength. The inherent nonlinearity of the evolution equations leads to significant coupling between the modes in the vicinity of the dominant wavelength. Numerical calculations that account for these coupling effects are in very good agreement with the experimental observations.

4:45 PM U2.9/JJ2.9/KK2.9

Dislocation Driven Surface Dynamics on Solids.

Sanjay V. Khare^{1,2}, S. Kodambaka^{1,2}, W. Swiech^{2,1}, K. Ohmori^{1,2}, I. Petrov^{2,1} and J. E. Greene^{1,2}; ¹Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois; ²Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, Illinois.

Using low-energy electron microscopy, we investigate the near-equilibrium dynamics of surface-terminated dislocations. We observe, in real time, the thermally-driven (1500-1700 K) nucleation and shape-preserving growth of spiral steps rotating at constant temperature-dependent angular velocities ($\omega(T)$) around cores of dislocations terminating on TiN(111) in the absence of applied external stress or net mass change. We measure ω as a function of spiral geometry, N₂ partial pressure, annealing time, and temperature.

We find that ω is independent of the local environment and ambient, and decreases linearly with time. From the temperature-dependent ω data, we obtain an activation barrier of 4.9 ± 0.3 eV for the growth of spirals. This phenomenon, attributed to point-defect migration from the bulk to the surface along dislocation lines, is both qualitatively and quantitatively different from step curvature-driven surface dynamics and "standard" Burton-Cabrera-Frank (BCF) spiral growth.¹ Our results demonstrate that dislocation-mediated surface roughening can occur even in the absence of deposition or evaporation, and provide fundamental insights into mechanisms controlling nanostructural stability. We expect that this process is general and that it occurs in other materials. ¹S. Kodambaka, S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, and J.E. Greene, *Nature* 429, 49 (2004).

SESSION U3: Poster Session
Monday Evening, November 29, 2004
8:00 PM
Exhibition Hall D (Hynes)

U3.1 High Frequency Phonon Modes in Nanoimprinted Gratings and Nanowires for Microelectronics Applications.

Colm M. Flannery^{1,4}, Sudook Kim¹, Ward Johnson¹, Stephanie Hooker¹, Christopher Soles², Ryan Hartschuh³, Alexandre Kisliuk³ and Alexei Sokolov³; ¹Materials Reliability, National Institute of Standards and Technology, Boulder, Colorado; ²Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland; ³Dept of Polymer Science, University of Akron, Akron, Ohio; ⁴Engineering Division, Colorado School of Mines, Golden, Colorado.

Structures for microelectronic and other applications are becoming increasingly important in the sub-100 nm range. However, structures of such size present serious problems to fabricate and inspect in a reliable and repeatable manner. Mechanical properties of the materials involved can become quite different from bulk or even micron-scale properties, and there is a serious lack of inspection techniques to characterize important properties, such as stiffness and density, as well as the dimensions and uniformity of the fabricated structures. In this work Brillouin light scattering (BLS) is used to extract the elastic properties of sub-100 nm lithographic features (parallel polymer lines and spacings) supported on a silicon wafer. BLS is a non-destructive, optical technique where incident laser light interacts with phonon modes present in the material inspected and photons are scattered with small changes in energy (or frequency) resulting from phonon-photon collisions. The frequency shifts are in the gigahertz range and indicate the different phonon modes present, which reveal the material's mechanical properties. An interesting aspect of this work is that the phonon wavelengths involved are of the order of the structure dimensions, meaning that a mode's velocity and propagation is sensitive to structure size. We show that BLS allows detection of both bulk and surface acoustic modes of lithographic nanostructures, allowing a comparison of the mechanical properties in sub 100-nm features to larger bulk-like samples. This allows us to probe vibrational modes in structures on a scale smaller than any previously inspected. Along with complementary measurements from specular X-ray scattering and surface acoustic wave spectroscopy, our results indicate that the mechanical properties do not deviate significantly from their bulk values for feature dimensions down to 80 nm. Interestingly, we detect new modes in these nanostructures (not present in the bulk) with frequencies below expected surface modes, and further attribute these to flexural Lamb-like vibrations confined within the nanostructured lines themselves. The ability to detect flexural modes in nanowires establishes BLS as a powerful non-contact, non-destructive tool to characterize mechanical properties of nanoscale features

U3.2 The Evolution of Surface Roughness During Homoepitaxial Growth on Patterned GaAs(001)-the Length Scale Dependence and Temperature Dependence.*

Tabatha Joan Garret^{1,2}, Tabassom Tadayyon-Eslami², Hung-Chih Kan² and Raymond J. Phaneuf²; ¹Chemistry, North Carolina State University, Raleigh, North Carolina; ²Laboratory for Physical Sciences, University of Maryland, College Park, Maryland.

We investigate the evolution of the surface roughness on patterned GaAs (001) surfaces [1] during homo-epitaxial growth at temperatures below and the above the pre-roughening transition temperature (PRT) [2]. Here, we concentrate on the effects of two characteristic lengths of the patterning on the initial surfaces. These parameters are the diameter and the center-to-center spacing of arrays of cylindrical pits patterned on GaAs(001) surfaces using photolithography. In order to investigate the effects of each parameter independently, we hold one length constant while varying the other systematically. The

surface topography after MBE growth at various thicknesses is characterized with atomic force microscopy (AFM) in air. We show the comparison of the evolution of the surface roughness with the parameters at temperatures both above and below the PRT. *Work supported by the Laboratory for Physical Sciences and an MRSEC [1] H.-C. Kan, et.al. Phys. Rev. Lett. 92, 146101 (2004) [2] V.P. LaBella, et.al. Phys. Rev. Lett. 84, 4152 (2000)

**U3.3
Stress Stability of Poly-SiGe and Various Oxide Films in Humid Environments.** Carrie W. Low¹, Brian L. Bircumshaw², Tatiana Dorofeeva¹, Gelila Solomon¹, Tsu-Jae King¹ and Roger T. Howe^{1,2}; ¹Electrical Engineering and Computer Sciences, University of California at Berkeley, Berkeley, California; ²Mechanical Engineering, University of California at Berkeley, Berkeley, California.

Reliability specifications require most MEMS thin films to have long-term material stability. Low processing temperature makes poly-SiGe a promising structural material for modular integration with electronics [1]. LPCVD and PECVD oxides are frequently used as sacrificial layers because of their high deposition rates at low deposition temperatures. In past research, results from the analysis of wafer curvature over time appeared to indicate that poly-SiGe films experience a stress drift in humid environments [2]. Recent results show that the residual stress of poly-SiGe films is, in fact, stable in ambient conditions. Due to RIE selectivity issues, SiGe is deposited on SCS wafers coated with oxide, and the backside SiGe films are stripped off for wafer curvature measurement. The measured stress of SiGe on LPCVD oxide become more tensile over time, but SiGe on thermal oxide is stable. Stress stability of different oxides is explored further with single layer film. The stress of the 450 °C LPCVD oxide becomes more compressive over time while stresses of 1050 °C dry and wet thermal oxides remain the same. The stresses of PECVD oxides deposited below 400 °C also drift towards more compressive, but SiH4-based PECVD oxide is more stable than TEOS-based PECVD oxide. LPCVD low temperature oxide (LTO) films are known to be porous and of poor quality [3]. Putting the LTO films in a desiccated environment arrests the stress drift, while annealing the films at 615 °C for five hours slows down the drift. Also, the drift profile is saturating over time. The above facts suggest that the absorption of ambient water into the LTO film is the major cause of the observed stress drift. As water is absorbed, the films become more compressive. Annealing the LTO films at 825 °C for one hour halts the stress drift completely. Hence, it would appear that annealing densifies the LTO and decreases the diffusion constant. Data of SiGe-on-LTO wafers indicates that SiGe is an effective barrier to moisture. When the backside SiGe and LTO films are both removed, the stresses of the topside films become stable. If the backside SiGe of two similar SiGe-on-LTO wafers is removed at different times, the drift profiles and absolute stresses of the wafers are nearly identical. This data suggests that the stress drift reported in [2] is due solely to the instability of the LTO films. The backside LTO films became more compressive, causing an apparent positive drift in the SiGe film stresses. To fully understand the stress drift, classic Stoney equation [4] will be used to relate wafer curvature to the stress of multiple thin films. Also, a model will be developed to explain the time dependence of the stress drift. References: [1] A. Franke et al., J. MEMS., 12, p. 160-171 (2003) [2] B. Bircumshaw, et al., Tech. Digest of MEMS04, p. 514-519 (2004) [3] M. Madou, Fund. Of Microfab., 2nd ed, CRC Press, p. 302 (2002) [4] G. Stoney, Proc. Roy. Soc London, A82, 172 (1909)

**U3.4
Electronic Excitations of Stable Fullerene-Like GaP Clusters.** Giuliano Mallocci^{1,2}, Giancarlo Cappellini^{2,3}, Guido Satta^{2,3} and Giacomo Mulas^{1,2}; ¹Osservatorio Astronomico di Cagliari, INAF, Capoterra (CA), Italy; ²Physics Department, Cagliari University, Cagliari, Italy; ³SLACS, INFN, Cagliari, Italy.

Quasiparticle corrections to the electronic energies have been calculated for small GaP fullerenes, a new class of nano-scaled materials recently predicted to be stable and to show spontaneous formation [1]. These clusters have been also characterized by us for their optical absorption spectra using Time-Dependent Density Functional Theory [2]. The comparison between single-particle and optical absorption spectra supports the evidence of strong excitonic effects with binding energy up to 3eV [3]. The quasiparticle corrected HOMO-LUMO energy gaps confirm the high stability yet predicted for such molecules with the use of ground-state computational schemes. The present results will enable the identification of the successful synthesis of such systems via optical absorption and quasiparticle spectra. [1] V. Tozzini, F. Buda, A. Fasolino, Phys. Rev. Lett. 85, 4554 (2000) [2] G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. 74, 601 (2002) [3] G. Cappellini, F. Casula, J. Yang, F. Bechstedt, Phys. Rev. B 56, 3628 (1997)

**U3.5
The Role of Surface Step in Stabilizing Surface Structures.**

Danxu Du¹, David J. Srolovitz¹ and Henny W. Zandbergen²; ¹Dept. of MAE, Princeton University, Princeton, New Jersey; ²Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg, Delft, Netherlands.

Surface steps induce elastic stresses along the surface and into the bulk of the material. These stresses can drive surface reconstructions and the introduction of other defects into/near the surface - including dislocations and point defects. These mechanically-induced forces lead to repulsion between these defects and surface steps in addition to traditionally understood attraction. This effect is a continuum analogy of Ehrlich-Schwoebel effect at atomic level. This analysis is applied to understand evanescent trapping of gold atoms near surface steps observed recently in the TEM. These results are further corroborated via molecular statics simulations. We also examine the morphological instability and evolution of surface domains under these forces, leading to the surface equivalent of particle splitting in bulk materials and providing a retarding mechanism for surface nanostructure coarsening.

U3.6

Structure of Si(001) surface and thin Ge layers on Si(001): Monte Carlo Simulations of Dimer Vacancy lines.

Antti Kuronen, Laura Juvonen and Ville Lilja; Laboratory of Computational Engineering, Helsinki University of Technology, Espoo, Finland.

One of the most common defect on the Si(001) surface is the dimer vacancy which can be created by ion bombardment, etching, or introducing contaminations. These defects have been observed to create clusters at lower concentrations and regular line structures at higher concentrations. This ordering is due to the elastic interactions between dimer vacancies. The initial stages of submonolayer growth of Ge on Si(001) are similar to Si homoepitaxy. As the Ge coverage increases the strain caused by the 4.2% lattice misfit between Si and Ge begins to affect the surface structure. The main strain relaxation mechanism at coverages in the range of 0.8-2 monolayers is the formation of dimer vacancies. Experimentally these have been observed to arrange in regular line structures due to their mutual repulsion. In this work we have studied the equilibrium structure of dimer vacancy lines on pure Si(001) and on submonolayer Ge thin films on Si(001) by means of Monte Carlo simulations. Dimer vacancies are assumed to be particles interacting via a pair potential which is calculated by using the semiempirical Stillinger-Weber potential. The structure of the surface is investigated as a function of temperature and vacancy concentration and the main differences between the homoepitaxial Si and heteroepitaxial SiGe systems are studied.

U3.7

Calculations of the Formation and Structure of Monolayer Island Arrays under Anisotropic Conditions. Gajendra Pandey and Robert V. Kukta; Mechanical Engineering, State University of New York at Stony Brook, Stony Brook, New York.

The continued miniaturization of electronic devices has driven a large research effort to develop new techniques for fabricating nanostructures. A nanostructure that has established widespread interest because of its technological significance is an array of well-organized material deposits on a substrate. These structures form spontaneously in certain epitaxial systems, but their degree of organization tends to be insufficient for many device applications. This paper addresses the potential of using anisotropies to enhance organization and produce various array structures. Focus is on in-plane anisotropies in surface stress and lattice mismatch between the film and substrate materials. Under isotropic conditions the arrays form as hexagonal cells. As individual cell domains have no orientational bias, they tend to form defects and possess only short-range order. A preferred orientation for island alignment due to anisotropy could enhance organization over large scales. The goal is to study the effect of anisotropy on the formation of arrays as they evolve towards a metastable state. The analysis treats monolayer islands as point sources of stress that interact through their elastic fields. The nature of the stress induced by an island is determined from a line defect model of surface steps. It is found that the point source model is accurate for island separations larger than about 5 times the island diameter. The system is evolved using a simple kinetic relation whereby an island moves with a velocity that is proportional to its energetic driving force, which depends on the position of all other islands in the system. Under anisotropic conditions the driving force causes islands to align in particular directions and, some cases, to attract each other. It is found that anisotropy can cause arrays to develop with islands arranged in rectangular cells or in a zigzag pattern.

U3.8

Nano-scale Stress and Compositional Analyses of Epitaxial

Silicon-Germanium Undulated Films. Chi-Chin Wu and Robert Hull; Materials Science and Engineering, University of Virginia, Charlottesville, Virginia.

Stress relaxation and composition re-distribution are two fundamental processes during growth of strained epitaxial Si_{1-x}Ge_x/Si(100) alloy layers. In this work, we will present both theoretical and experimental approaches to investigate the inter-relation between these mechanisms. Stress values in undulated layers were calculated via the Finite Element Method by assuming a sinusoidal surface geometry. They were investigated as functions of undulation wavelengths and amplitudes between the trough and peak regions. For example, with a 50nm layer of x=0.3 having undulations of 250nm wavelength and 40nm amplitude, the compressive stress is twice as high in the trough regions than in the peak regions. To explore compositional redistribution in response to these laterally varying strain fields, a new experimental approach has been developed to determine local germanium concentrations for such undulated alloy layers. An etchant consisting of HNO₃ (70%): H₂O: HF (0.5%), 25:35:5, at 28°C etches Si_{1-x}Ge_x/Si(100) alloy layers at a rate of several nanometers per minute. The etching rate increases with increasing germanium concentration in the alloy layer. Such etching experiments can thus be applied to etch alloy layers with compositionally varying undulations on the free surface and utilized to quantify the local germanium concentrations. For an alloy layer with x=0.3, the germanium contents from this analysis are estimated to be about 20% richer and depleted in the peak and trough regions, respectively. In-situ annealing experiments via transmission electron microscopy are also under way to experimentally measure local stress variations by observation of velocity variations when a dislocation line propagates through the undulation stress fields. Such correlations are possible because of the extensive measurements we have previously made correlating local stress to dislocation velocities in these systems.

U3.9

Abstract Withdrawn

SESSION U4: Quantum Dots and Nanopatterned Surfaces

Chairs: Cristian Ciobanu and Leo Miglio
Tuesday Morning, November 30, 2004
Room 210 (Hynes)

8:30 AM U4.1

Effect of Interdiffusion of Si on Morphological Evolution of SiGe Quantum Dots - A Phase Field Study.

Ramanarayan Hariharaputran and Vivek B. Shenoy; Division of Engineering, Brown University, Providence, Rhode Island.

The influence of Si interdiffusion on the evolution of SiGe nanostructures during deposition and post deposition annealing was studied using phase field model. The quantum dots formed due to Asaro-Tiller-Grinfeld (ATG) instability is modeled using a ternary phase field model with A rich α phase as the film, B rich β phase as the substrate and a vapor phase. Using intermixing or unmixing characteristics of the free energy, different stages of growth and annealing process have been addressed. Attempts have been made to understand many recently observed experimental features such as trench formation, inhomogeneous composition and quantum rings using this model. We characterize the evolution as a function of kinetic parameters such as surface and bulk diffusion coefficients of different species, material parameters such as elastic properties and operational parameters like deposition rate.

8:45 AM U4.2

Extended Shape Evolution of Low Mismatch SiGe Alloy Islands on Si (100). Eli Sutter¹, Peter Sutter¹ and James Bernard²;

¹CFN, Brookhaven National Laboratory, Upton, New York; ²Physics, Colorado School of Mines, Golden, Colorado.

Strain-induced self-assembly of coherent Ge (SiGe) quantum dot (QD) islands on Si(100) has attracted considerable interest recently as an elegant route for creating large-scale arrays of nanostructures. An important factor for the proposed use of such self-assembled QDs in electronic devices is achieving a detailed knowledge of the island shapes as a function of volume at different levels of lattice mismatch strain. So far much effort has focused on investigating the shape evolution of coherent Ge islands that form spontaneously during Ge/Si(100) heteroepitaxy to relax part of the 4% lattice mismatch strain. In their evolution with increasing Ge coverage, these faceted islands assume a sequence of different shapes. Initially they are pyramids terminated by shallow {105} facets ("huts", [1]). At larger volume, they transform into multifaceted "domes" with higher aspect ratio and additional steeper facets [2,3]. For Ge and for SiGe alloys with high Ge content, the sequence of coherent island shapes ends

with the dome morphology as lattice mismatch strain is further relaxed plastically by dislocations [4]. Low mismatch, dilute SiGe alloys with Ge content of 20% or less are believed to undergo an identical sequence of morphological transitions, the only difference being an increase in length scale due to the reduced lattice mismatch strain. Here we report on observations that disprove this assumption, showing a different and more complex strain relaxation pathway for dilute SiGe alloys. Using scanning tunneling microscopy and cross-sectional transmission electron microscopy we have documented an extended sequence of coherent 3D island shapes in the heteroepitaxy of dilute SiGe alloys on Si(100) [5]. Following the known "hut" and "dome" islands, a new "barn" shape is reached via a shape transformation, in which steep {111} facets are introduced. After the initial formation of small {111} facets, the "barn" shape evolves via a continuous increase in {111} coverage. In comparison with higher-strain systems such as Ge/Si(100), our observations demonstrate a significantly altered competition between the two fundamental strain relaxation mechanisms in 3D islands - coherent shape evolution and dislocation nucleation - in the limit of low lattice mismatch strain. References: [1] Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. 65, 1020 (1990). [2] G. Medeiros-Ribeiro, A. M. Bratkovski, T. I. Kamins, D. A. A. Ohlberg, and R. S. Williams, Science 279, 353 (1998). [3] F. M. Ross, R. M. Tromp, and M. C. Reuter, Science 286, 1931 (1999). [4] E. Sutter, P. Sutter, P. Zahl, P. Rugheimer, and M. G. Lagally, Surf. Sci. 532, 785 (2003). [5] E. Sutter, P. Sutter, and J. E. Bernard, Appl. Phys. Lett. 84, 2262 (2004).

9:00 AM U4.3

Formation of Si/Ge Nanostructures on the Atomic Level.

Bert Voigtlander, Vasily Cherepanov, Neelima Paul and Josef Mysliveček; Forschungszentrum Jülich, Jülich, Germany.

The step-flow growth mode is used to fabricate two-dimensional Si and Ge nanowires with a width of 3.5 nm and a thickness of one atomic layer (0.3 nm) by self-assembly on a Si(111) surface. Alternating deposition of Ge and Si results in the formation of a nanowire superlattice covering the whole surface. One atomic layer of Bi terminating the surface is used to distinguish between the elements Si and Ge. A difference in apparent height is measured in scanning tunneling microscopy (STM) images for Si and Ge, respectively. Also different kinds of two-dimensional Si/Ge nanostructures like alternating Si and Ge nanodots and nanorings having a width of 5-10 nm were grown. The reason for the height difference observed in STM will be discussed. The method to distinguish between Si and Ge allows to study the stability of these nanostructures upon annealing and gives access to intermixing on the nanoscale and to identify the fundamental processes giving rise to the intermixing.

9:15 AM U4.4

Kinetic Control of Dome Cluster Composition by Varying Ge Deposition Rate. Emily McDaniel¹, Jeff Drucker^{1,2}, P. A. Crozier²,

Qian Jiang¹ and David J. Smith^{1,2}; ¹Department of Physics and Astronomy, Arizona State University, Tempe, Arizona; ²Center for Solid State Science, Arizona State University, Tempe, Arizona.

The mean size of dome clusters grown by molecular beam epitaxy of pure Ge onto Si(100) at substrate temperatures, T, from 450 to 650°C is deposition rate dependent. For samples with nominal Ge coverages near 8 ML (1 ML = 6.78×10^{14} atoms/cm²) and deposition rates between 0.4 and 17 ML/min, higher deposition rates decreased the mean dome diameter and increased the dome areal density. For growth at T=650°C, the mean dome diameter varied between 100 and 70 nm; for T=550°C, between 55 and 51 nm; and for T=450°C, between 40 and 37 nm. Integrated island volumes measured using atomic force microscopy are greater than can be accounted for by the Ge coverage measured using Rutherford backscattering spectrometry, indicating Si interdiffusion into the domes. By this measure, the Ge content of the dome clusters rises with increasing deposition rate. Also indicative of the increase of Ge content with deposition rate is the decrease in the pyramid-to-dome transition volume with increasing deposition rate. Preliminary, quantitative, nm-resolved electron energy loss spectroscopy (EELS) measurements taken in a scanning tunneling electron microscope confirm these results. For samples grown at T=650°C with rates of 1.4 ML/min and 17.5 ML/min, EELS of dome clusters indicates 60% Ge and 70% Ge dome compositions, respectively. These results indicate that dome cluster composition may be kinetically controlled by varying the Ge deposition rate.

9:30 AM U4.5

Kinetics and Thermodynamics at the Ge(105) Surface: Theory and Consequences on Ge-Dot Growth on Si(001).

Silvia Cereda, Dmitri B. Migas, Francesco Montalenti and Leo Miglio; Dipartimento di Scienza dei Materiali, University of Milano-Bicocca, Milano, Italy.

Ge pyramids grown on Si(001) are bound by {105} facets. A complex,

Rebonded-Step (RS) reconstruction takes place at such facets, deeply changing the overall atomic configuration of the outermost layers. Based on DFT calculations, we show that the Ge(105)RS surface displays a very peculiar behavior in terms of both thermodynamic and kinetic properties. The surface energy, indeed, is decreased by compression [1], while adatom diffusion is fast and isotropic [2]. Consequences on recent experimental evidences concerning Ge-dot growth on Si(001) are discussed. Furthermore, we present an atomic-scale model for next-layer nucleation on such surface, demonstrating that few, low-energy (well activated at typical experimental temperatures) diffusion processes are sufficient to keep the exact reconstruction during growth.

9:45 AM U4.6

Real-Time Growth and Coarsening Dynamics of Ge/Si(100) Nanostructures Using Elevated Temperature Scanning Tunneling Microscopy. Michael Reynaldo McKay¹ and Jeff

Drucker²; ¹Science and Engineering of Materials, Arizona State University, Tempe, Arizona; ²Physics and Astronomy, Arizona State University, Tempe, Arizona.

Growth and coarsening dynamics of Ge/Si(100) nanostructures were monitored using movies produced from real-time, elevated temperature scanning tunneling microscope images. Gas-source molecular beam epitaxy from digermane at 0.1 ML / min onto Si(100) at temperatures near 500 deg C produced mixed hut and pyramid cluster ensembles. Growth temperature annealing revealed that pyramid clusters are more stable than hut clusters with larger volumes. Large (> 1 micrometer diameter), low chemical potential clusters deplete the surface of Ge adatoms as evidenced by the existence of 800 nm-wide denuded zones devoid of smaller clusters. Outside of these denuded zones the pyramid cluster density is nearly unchanged during 15 hr anneals at 500 deg C. During growth, wetting layer formation proceeds through phases distinguished by the Ge adatom diffusion length upon the increasingly rough Ge/Si surface. A transition between step-flow growth and nucleation of 2-D islands may be kinetically influenced through variations in deposition flux and substrate temperature. Wetting layer (WL) coarsening dynamics differ dramatically between 475 and 500 deg C. At the lower end of the temperature range, the WL appears static when compared to the rapid (on the 5 min per frame timescale) motion at 500 deg C. The WL does not coarsen during a 15 hr anneal at T=475 deg C unlike the obvious coarsening during the 500 deg C anneal. Additionally, the WL formed at 500 deg C is coarser with larger terrace sizes and is elongated in the direction of missing dimer defects. This elongation is less pronounced in the WL formed at 475 deg C.

10:30 AM U4.7

Semiconductor Nanocrystal Quantum Dots on Single Crystal Semiconductor Surfaces: Stability and Structure. Atul Konkar¹,

Siyuan Lu¹, Anupam Madhukar¹, Steven Hughes² and A. Paul Alivisatos²; ¹Departments of Materials Science & Physics, University of Southern California, Los Angeles, California; ²Department of Chemistry, University of California, Berkeley, California.

Semiconductor nanocrystals quantum dots (NCQDs), prepared via colloidal solution methods, exhibit high optical quality and emission wavelengths that can be tuned over a wide range. Successful integration of NCQDs onto/into single crystalline semiconductor substrates/matrices will enable wide technological application of NCQDs as the active element in optoelectronic devices. As a first step we have investigated the stability and structure of InAs NCQDs on GaAs (001) substrates. The colloidal InAs NCQDs in a toluene solution are covered by tri-octyl phosphine (TOP) ligand molecules that acts as surfactant and also passivate the surface. The interaction and bonding between the NCQDs and *clean* GaAs (001) surface, and the NCQD stability were investigated using Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). In contact mode AFM, the lateral shear force on the NCQDs can be adjusted by appropriate choice of the normal force, tip/cantilever geometric structure, and the horizontal tip velocity. The AFM studies show that the NCQDs on GaAs are only weakly physisorbed since, even after annealing at 200°C for an hour, the NCQDs can be freely moved on the substrate with minimum shear force. Even after annealing at temperatures > 300°C, only 50% of the NCQDs exhibit significant covalent bonding with the substrate and are able to withstand the shear force. Plan-view, high-resolution TEM and electron diffraction studies of as-deposited NCQDs on electron transparent GaAs(001) membranes show that the NCQDs do not have any epitaxial relationship with the substrate. Significant NCQD size reduction is observed for annealing above 300°C. We will elucidate the role of TOP ligand molecules in screening the interactions between the NCQD and the substrate. The NCQD stability will be discussed in terms of the traditional notions of surface curvature induced capillarity and the lower thermodynamic stability of nanocrystals i.e. the 'Kelvin effect'. The role of the substrate surface will be discussed. This work was supported by the DoD, under the DURINT (Defense

10:45 AM U4.8

Differing Roles of Substrate Steps in Dewetting of Thin Ag Films on Si(111) and Ru(0001). Konrad Thuermer¹, Wai Li Ling¹, Norman C. Bartelt¹, Kevin F. McCarty¹, Ellen D. Williams² and Janice E. Reutt-Robey²; ¹Sandia National Laboratories (CA), Livermore, California; ²University of Maryland, College Park, Maryland.

Hetero-epitaxial films often do not wet their substrates at equilibrium. Instead, three-dimensional (3-D) islands, relaxed to bulk lattice parameters, form to lower free energy, exposing the bare substrate or a very thin wetting layer (Stranski-Krastanov systems). During the dewetting process mass flows from the film's thinner regions to its thicker regions. We discuss this dewetting process for the Stranski-Krastanov systems Ag (or Cu)/Ru(0001) and Ag/Si(111). The initial configuration was created by depositing continuous 1-nm-thick Ag (or Cu) films at temperatures below the onset of dewetting. We then tracked the dewetting process upon annealing in real time using low-energy electron microscopy (LEEM) for Ag (or Cu)/Ru(0001) and variable-temperature scanning-tunneling microscopy (STM) for Ag/Si(111). We found that the two systems behave extremely differently. In particular, substrate steps enable dewetting in one case (Ag and Cu/Ru), but inhibit it in the other (Ag/Si). Our real-time observations showed that Ag and Cu films de-wetted the Ru substrate by 3-D islands migrating "down" substrate steps. We have observed islands thicken by more than 50 atomic layers in this way. This downhill-migration process allows 3-D growth to occur in a way that avoids the nucleation barrier associated with forming 2-D islands on top of dislocation-free 3-D islands. Indeed, without substrate steps this nucleation barrier is not surmounted, and no 3-D Ag or Cu islands formed on Ru. While the Ru steps allowed the Ag and Cu islands to thicken without having to nucleate new layers, the nucleation barrier in the Ag/Si system plays a less prominent role because of the film roughness and the presence of dislocations in the 3-D islands. In fact, instead of facilitating dewetting, Si substrate steps actually obstructed the Ag dewetting. Our observations suggest that the dewetting process is controlled by mass diffusion and that substrate steps serve as diffusion barriers for Ag atoms. That is, the substrate steps limit the feeding areas of growing 3-D crystals. A crystal on a high-step-density substrate draws material from a narrow stripe and therefore material has to travel a longer path to grow a crystal of a given size, compared to crystal on a wide terrace. Since mass diffusion is significantly faster on the wetting layer (which has a reconstructed $\sqrt{3}\times\sqrt{3}$ structure) than on the thicker layers, the mass-transport rates change during dewetting. The overall process is very complex even though no silicide formation occurs and the film has a vanishing net strain. This research was supported by the Office of Basic Energy Sciences, Division of Material Sciences, U.S. Department of Energy, under Contract No. DE-AC04-94AL85000.

11:00 AM U4.9

Facet Formation on Si(124) Surfaces. Kenji Ohmori, Suneel Kodambaka, Sanjay V. Khare, Javier Barenó, Vania Petrova, Wacek Swiech, Joseph E. Greene and Ivan Petrov; Materials Research Laboratory and Department of Materials Science, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Self-assembly of position- and shape-controlled nanostructures can be achieved by preparing template surfaces with self-organized periodic structures which derive from step bunching, facet/domain formation, and strain. We have chosen Si(124) substrates, which provide suitable template structures for several- μm -long Ge nanowire growth, as a model system to develop a fundamental understanding of the thermodynamics of surface facetting. Using in-situ ultrahigh vacuum high-temperature scanning tunneling microscopy, we investigate facet formation on Si(124) surfaces as a function of temperature T_s from 500 to 900 °C. We observe four temperature regions: (1) at 500 °C < T_s < 750 °C, the Si(124) surface forms a long straight hill-and-valley structure composed of (113) and (157) facets with a period of tens of nanometers (two-phase coexistence); (2) at 750 °C < T_s < 850 °C, areal fractions of (113) and (157) decrease with the appearance of a third disordered rough facet which changes its facet indices as a function of T_s in order to maintain the mean surface (124) orientation (three-phase coexistence); (3) at 850 °C < T_s < 900 °C, with the disappearance of (157) facet, the surface is again two-phase consisting of (113) and the third rough facet; (4) the (113) facet vanishes and only the third facet remains with the index coinciding with (124) at T_s > 900 °C. These results can be understood in terms of the competition between surface energies and elastic interactions.

11:15 AM U4.10

Step roughness reversal on Si(001) under compressive strain. Cristian Ciobanu, Vivek Shenoy and L. Ben Freund; Division of

We report the strain dependence of the energies of kinks on monatomic-height steps (SA, SB) on the Si(001) surface. Our calculations indicate that the energy of kinks on SA steps decreases with compressive strains, while that of kinks on SB steps increases. Since in the absence of strain SA steps are straight and SB steps are rough, these results indicate a reversal of step roughness under applied compression, in agreement with the experimental observations of Wu et al. (Phys. Rev. Lett. 74, 574 (1995)).

11:30 AM U4.11

Energetics and Kinetics of Epitaxial Island Formation on Lattice Mismatched Patterned Substrates.

Noah Donald Machtay and Robert V. Kukta; Department of Mechanical Engineering, State University of New York at Stony Brook, Stony Brook, New York.

Spontaneous self-assembly of nanostructures has been a problem of long-standing interest for fabricating advanced electrical and optical devices. One approach towards controlled self-assembly is epitaxial growth on topographically patterned substrates. The substrate shape addressed here is a periodic array of rectangular mesas. Strained-layer growth on such substrates has been observed to form as islands at various positions on a mesa, on the edges, in the center, or as a combination of these. The purpose of this investigation is to discern whether these morphologies are driven by energetic or kinetic mechanisms. An energetic analysis is done under the assumption that the system free energy consists of surface free energy and strain energy. Strain arises due to a lattice mismatch between the film and substrate materials. The film and substrate are treated as two-dimensional linearly elastic solids with similar elastic properties. Strain energy is evaluated using finite element analysis. Under the constraint of fixed volume, various island arrangements and shapes are compared to determine low energy configurations. Islands are assumed to have the shape of a circular arc, and systems of one, two, and three islands are considered with positions at the center or edges of the mesa. For symmetric cases, depending on mismatch strain, surface energy, and volume, it is found that either the single centered island configuration or the configuration with two edge mounted islands may be favored. Allowing for asymmetry, a single island placed on one edge of the substrate mesa is generally the low energy configuration. This occurs because the edge of a raised mesa is highly compliant and admits relaxation of a large amount of mismatch strain. As symmetric edge mounted islands have been observed experimentally, is it of particular interest to determine whether a two edge mounted island formation could form via kinetic processes and if there is an energetic barrier preventing such a system from transitioning to the lower energy single edge island state. The case of one edge mounted island translating towards the other to ultimately coalesce into a single island is considered to determine if an energetic barrier existed for that process. Spontaneous mass transfer between islands is also addressed. Kinetic simulations of morphological evolution during combined deposition and surface diffusion is also conducted in order to understand whether observed morphologies are metastable states or slowly evolving nonequilibrium states.

11:45 AM U4.12

Efficient Phase-Field Simulation of Faceted Quantum Dot Formation in a Strained Heteroepitaxial Film. Steven Wise, John Lowengrub and Junseok Kim; Mathematics, UC, Irvine, Irvine, California.

A Cahn-Hilliard type phase field model is employed to study the formation of quantum dots in coherently strained, heteroepitaxial thin films. The model includes the effects of strong anisotropic surface energy, allowing for the formations of primary and secondary faceting of the quantum dots, and the effects of complex, anisotropic elastic interaction with the substrate. Substrate patterning is studied as a mechanism for ordering the quantum dots, with both topographic and strain-modification (e.g., through embedded coherent inclusions and defects) patternings considered. The model allows for a unified treatment of a number of current design problems, including the formation of quantum dot superlattices during multi-stage deposition; quantum rings, wires, and fortresses; and planar arrays of quantum dots. In this talk we present two and three-dimensional dynamical simulations. We also give some details of the sophisticated the multigrid/implicit time integration scheme for solving the Cahn-Hilliard model.

1:30 PM U5.1

Shape-Dependent Catalytic Properties of Transition Metal Nanoparticles and the Effect of Colloidal Catalysis on the Size and Shape of the Nanoparticles. Radha Narayanan and Mostafa A. El-Sayed; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Since nanoparticles have a small surface-to-volume ratio compared to bulk materials, they are attractive to use as catalysts. Tetrahedral shaped nanoparticles are especially attractive to use due to the high fraction of surface atoms on their corners and edges. Tetrahedral, cubic, and spherical shaped platinum nanoparticles are used to catalyze the electron transfer reaction between hexacyanoferrate (III) and thiosulfate ions. It is observed that during the very early part of the reaction that the tetrahedral nanoparticles are the most catalytically active, while the cubic nanoparticles are the least catalytically active. The catalytic activity of the spherical nanoparticles is intermediate to that of the tetrahedral and cubic nanoparticles. The observed catalytic activities are correlated with the fraction of atoms available on the corners and edges of each nanoparticle shape. It is also important to know what happens to the three different shaped nanoparticles during the course of the electron transfer reaction since the surface atoms of nanoparticles are very active, which could also make them unstable. The stability of tetrahedral, cubic, and spherical platinum nanoparticles during the course of the electron transfer reaction has also been investigated. It is observed that the dissolution of surface platinum atoms on the corners and edges occurs in both tetrahedral and cubic nanoparticles, while the rate of dissolution is faster for tetrahedral nanoparticles. The shape changes results in the catalytic activity changing during the course of the electron transfer reaction. The use of spherical palladium nanoparticles and tetrahedral platinum nanoparticles to catalyze the Suzuki reaction between phenylboronic acid and iodobenzene, a more harsh reaction, results in changes in the size and shape of the nanoparticles. Possible reasons for the changes in the size and shape of the nanoparticles during the Suzuki reaction will be discussed.

1:45 PM U5.2

Stability Study of Highly Dispersed Au Clusters Produced on Sputter Defected TiO₂ (110), Evidence from SEM and Olefin TPD. Yong Yang, Sung-Hyeon Baeck and Eric McFarland; University of California, Santa Barbara, Santa Barbara, California.

Fabrication of size selected nanoparticles on flat substrates is important for several applications including: chemical vapor deposition (CVD) synthesis of single walled carbon nanotubes (SWNT). TiO₂ supported Au nanoclusters are of great interest for high activity partial oxidation materials such as olefin epoxidation. In this study, ideal fully oxidized TiO₂ (110) surfaces were prepared in UHV then defected by controlled exposures to Ar (250 eV) ion sputtering. Ideal, control samples were prepared as well as samples with 0.1%, 1% and 10% of their surface area uniformly sputtered. Au (<1A) is evaporated on each surface and the existence of Au is confirmed by XPS. After heating to 700 K, SEM results show that Au sinters to large clusters (> 20 nm) on control samples while on sputtered TiO₂, nanoparticulate Au is observed with sizes smaller than resolution limit. The density of clusters is correlated to that of the surface defected sites and decrease of cluster size is observed with increased sputtering time. We propose that Au deposited on a sputtered surface is immobilized at defect sites. As a result, olefin metal interaction energy is expected to increase as the cluster size decreases. This is supported by TPD results after exposure to propylene at 100 K. On the ideal surface, two desorption peaks are observed, one is at 150 K which is attributed to desorption of propylene from TiO₂ sites and the other is at 210 K from Au/TiO₂ sites. A distinct shift of the 210 K peak to higher temperature with sputtering is observed (210 K -> 270 K (1%) and 300 K (10%)). Similar behavior is observed with ethylene desorption. By using the Au/TiO₂ desorption peak as an indirect indication of the cluster size, the size stability of nanocluster formed on defects vs. energy of sputtering ion and substrate temperature may be studied.

2:00 PM U5.3

Size Dependent Changes of the Local Structure in Dodecanethiol-Stabilized Gold Nanoparticles. Anatoly Frenkel¹, Talia Harris¹, Sarah Nemzer¹, Ilana Pister¹, Louise Soussan¹, Yuan Sun² and Miriam Rafailovich²; ¹Stern College for Women, Yeshiva University, New York, New York; ²Materials Science and Engineering, State University of New York, Stony Brook, New York.

Thiol-stabilized gold nanoparticles have been predicted to adopt regular polyhedral shapes (e.g., cuboctahedron, icosahedron, truncated octahedron) as their size changes. However, experimental confirmation of these models is lacking, in part due to inability to control the size of the small particles, or due to the lack of adequate techniques to study their structure. We employed one-phase and two-phase synthetic routes to prepare dodecanethiol-stabilized gold

nanoparticles. For both procedures, we varied the gold-thiol ratio, from $x = 1/6$ to $1/3$ to $1/1$ to $3/1$ to $6/1$, in order to control the mean particle size. The average sizes of the particles prepared by both methods varied monotonically with x , the smallest (1 nm) being the particles prepared with $x=1/6$. To study systematic changes of the particles structure with the particle size, we analyzed them by X-Ray Absorption Fine-Structure technique at the National Synchrotron Light Source at Brookhaven National Laboratory. The combination of results obtained by TEM and XAFS allowed us to compare the sizes, metal core structures, Au-Au and Au-S bonding properties, as well as thiol coverage and sulfur adsorption mechanisms in the particles made by these two routes.

2:15 PM U5.4

On the Chemical Stability of Silver Nanoparticles in Ambient Conditions. Matthew David McMahon¹, Rene Lopez¹, Kenneth E. Schriver¹, Harry M. Meyer², Anthony B. Hmelo¹, Robert H. Magruder¹, Robert A. Weller¹, Leonard C. Feldman¹ and Richard F. Haglund¹; ¹Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; ²Metals and Ceramics Division, Oak Ridge National Laboratories, Oak Ridge, Tennessee.

The optical response of ordered arrays of noble metal nanoparticles have recently been experimentally characterized and theoretically modeled for applications ranging from nonlinear optics to biological sensing. Chemical and mechanical stability of the nanoparticles (particularly silver nanoparticles) under ambient conditions is a critical and often overlooked characteristic that will greatly affect the applicability, cost, and ease of deployment of surface plasmon resonance technologies. We measured spectra from an ordered $50 \times 50 \mu\text{m}^2$ square array of lithographically prepared silver nanoparticles in ambient over time intervals ranging from hours to days. The nanoparticles were disk-like, with radius 30 nm and height 20 nm, and the interparticle center-to-center spacing within the array was 162 nm. The optical resonance of the array redshifted nearly linearly (at a rate of 1.5 nm/hr) over a 2-day time span; the resonance peak also broadened and its amplitude decreased. Scanning Auger spectroscopy was used to characterize the surface elemental composition and yielded definitive evidence of sulfur contamination of the silver nanoparticles. The resonance shift is attributed to chemical instability of the nanoparticles, which most likely reacted with ambient levels of H₂S. Scanning electron micrographs showed that chemical changes correlated with mechanical deformation of the nanoparticles. We discuss various means of stabilizing the position, height and width of the resonance peak, including annealing the arrays and/or coating them with any of several inert dielectrics.

2:30 PM U5.5

Enhanced Mutual Solubility in Cu-Ag Alloy Nanoparticles Synthesized by Inert Gas Condensation. S. Ismat Shah¹ and Abdullah Ceylan³; ¹Materials Science and Physics, University of Delaware, Newark, Delaware; ²Materials Science and Engineering, University of Delaware, Newark, Delaware; ³Physics and Astronomy, University of Delaware, Newark, Delaware.

Cu-Ag alloy nanoparticles were prepared by Inert Gas Condensation (IGC) in which metal flux, obtained by the evaporation of high purity Cu and Ag wires from a tungsten boat, is condensed in the presence of He gas. Structural properties of the samples prepared at different temperature and pressure were investigated by using x-ray diffraction (XRD), transmission electron diffraction (TEM) and selected area diffraction pattern (SADP) analyses. X-ray diffraction patterns showed that particles were phase separated. According to the particle size values obtained by Scherer's law, there is no systematic change on the size of either Cu or Ag particles in the temperature range between 1020 °C and 1210 °C. By using lattice constant values and Vegard's law, it was realized that there was 6% Cu in the Ag matrix. This is much higher than the equilibrium solid solubility limit of Cu in Ag. Electron diffraction images not only revealed that particles were soft agglomerated but also showed results consistent with the XRD results regarding phase separation. Individual diffraction rings of the Cu and Ag observed on the SADP images. A model for the enhancement in the solid solubility limit will be presented.

3:15 PM *U5.6

Fundamental Sintering Studies of Metal Nanoparticle Arrays. Christopher John Kiely¹, Roger Ristau¹, Martin Harmer¹, Irshad Hussain² and Mathias Brust²; ¹Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania; ²Center for Nanoscale Science, Liverpool University, Liverpool, United Kingdom.

Since the realization that nanoscale metal and semiconductor particles exhibit unusual size-dependant properties, there has been great interest in using these particles as the building blocks for new 'bulk' materials with novel characteristics. Our research effort revolves around using the chemical interactions between ligand stabilized metallic nanoparticles to cause them to self-assemble into 1-D strings,

2-D films and 3-D supercrystals. The solid state sintering of such self-assembled nanoparticle arrays at first sight seems counterproductive. However, there are some instances when there are definite benefits to being able to controllably sinter self-assembled nanoparticle arrays into larger entities (e.g. the sintering of self-assembled strings of nanoparticles into continuous nanowires). Although the science of sintering of micron-scale metal and ceramic particles is very well developed, almost nothing is known about the fundamentals of sintering processes on the nanoscale, since this is a regime where the melting point of the nanoparticles are size-dependant and diffusion length scales are much reduced. We have ongoing experimental and theoretical research being carried out this area with the aim of gaining a fundamental understanding of the parameters that determine whether a nanoparticle system is prone to sintering by coarsening or densification. In this presentation, we describe how systematic sintering studies of arrays of ligand stabilized Au, Pt, Pd and Rh nanoparticles are allowing us to establish a basic understanding of how (i) particle size, (ii) particle melting temperature, (iii) particle array configuration, (iv) substrate identity, and (v) heating rate affect the nature of the nanowire or nanopattern formed. In-situ observations of dynamic nanoparticle sintering processes in a transmission electron microscope, along with critical comparisons to the well-known sintering phenomena that occur between micron-scale particles, form the cornerstones of our analytical approach to this problem. This research is supported by NSF under grant DMI-0304180, and the Pennsylvania Department of Community and Economic Development under contract 20-906-0009.

3:45 PM U5.7

Stability and structural transition of gold nanowires under surface stresses. Jiankui Diao¹, Ken Gall¹, Martin Dunn¹ and Michael I. Haftel²; ¹Department of Mechanical Engineering, University of Colorado, Boulder, Colorado; ²Nanostructure Optics Section, Naval Research Laboratory, Washington, DC, District of Columbia.

Researchers have demonstrated, through both experiments and analysis, that the structure and properties of nanometer-scale materials can be quite different than those of bulk materials due to the effect of free surfaces. We use atomistic simulations to investigate the stability and structure of gold nanowires under their own surface stresses. The stability of gold nanowires depends on wire size, initial orientation, exposed side surfaces, boundary conditions, temperature, initial cross-sectional shape and potentials used. Atomistic simulations with modified embedded atom method (MEAM) potential reveal that, for wires with a <100> initial crystal orientation and {100} side surfaces, surface stresses induce phase transformation from a face centered cubic (fcc) structure to a body centered tetragonal (bct) structure for very small nanowires and reorientation from an fcc <100> nanowire into an fcc <110> nanowire for relatively larger wires. In embedded atom method (EAM) and surface embedded atom method (SEAM) simulations, surface stresses induce yielding and reorientation from an fcc <100> nanowire into an fcc <110> nanowire below critical sizes. The difference in the instability mechanisms and the final structures is rooted in the differences in the unstable stacking fault energy and orientation dependence of electron density in the potentials. The existence of the bct phase is confirmed by first principle calculations.

4:00 PM U5.8

Real time PEEM of the Growth and Decay of DySi₂ Nanowires on Si(001). Anderson Sunda-Meya, Matthew C. Zeman, W. C. Yang, Lena Fitting and R. J. Nemanich; Physics, North Carolina State University, Raleigh, North Carolina.

Nanowires of DySi₂ were grown on a Si(001) substrate through UHV deposition of varying monolayers of dysprosium, followed by annealing at temperatures up to 1100 °C. In situ and real time monitoring of the formation, growth and decay of the silicide nanowires was performed by photo electron emission microscopy (PEEM) using mercury arc excitation. Direct observation combined with ex-situ AFM measurements were used to analyze the wire growth dynamics, their ordering, shape and size. We report on the decay of nanowires and their dependence on their initial width. Upon annealing, the width of thin wires (width 20 nm) remains constant while the length decreases with time. Meanwhile wider nanowires (width 200-300 nm) tend to break into sections with annealing. Furthermore, some wires are found to be thermally stable up to 1100 °C. We model these effects in terms of the epitaxial structure and surface and interface energetics. *Research supported by the NSF and the AFOSR through the MFEL program.*

4:15 PM U5.9

Growth of Nanowires of β -Na_xV₂O₅ by Metalorganic Chemical Vapor Deposition from Vanadyl Acetylacetonate. M.B. Sahana and S.A. Shivashankar; Indian Institute of Science, Bangalore, Karnataka, India.

β -Na_xV₂O₅ is a low-dimensional material with interesting electrical and magnetic behavior, which critically depends on the value of x. β -Na_{0.33}V₂O₅ exhibits three phase transitions as a function of temperature: a sodium-ordering transition at ≥ 240 K accompanied by a doubling of the unit cell along b-axis a metal-insulator transition at ≥ 136 K involving a tripling of the unit cell and a paramagnetic to -canted antiferromagnetic transition at ≥ 22 K. In this work, we report the growth on glass substrates of nanowires of β -Na_xV₂O₅ measuring 20-200 nm in diameter and 10-30 μ m in length, by metalorganic chemical vapor deposition using the β -diketonate complex, vanadyl acetylacetonate, as precursor, but without the use of either templates or catalysts, by exploiting its crystal structure anisotropy. Such growth takes advantage of the tendency for surface energy minimization, which promotes oriented growth on smooth amorphous substrates. The formation of β -Na_xV₂O₅ on glass is due to the reaction of the precursor with the substrate. Films consisting of nanowires of β -Na_xV₂O₅ with a preferred orientation along (h0l) are formed only at 550°C, whereas those deposited at 540°C comprise a mixture of nanowires (β -Na_xV₂O₅) and platelets (V₂O₅). Films deposited at lower temperatures are less crystalline and comprise a mixture of different vanadium oxides. Annealing at 550°C shows β -Na_xV₂O₅ to be volatile. Further, it is observed that nanowires are formed only in the narrow temperature range 540-550°C, and that there is a critical dependence of the formation of nanowires on the balance between the CVD growth rate and the evaporation rate of the film. Secondary ion mass spectrometry (SIMS) of thin films comprising nanowires and Rutherford backscattering spectrometry (BS) studies of vanadium oxide films deposited at different temperatures elucidate the factors leading to the formation of nanowires of β -Na_xV₂O₅. SIMS analysis shows the presence of higher percentage of sodium at the surface than at the interface of the film and the substrate. It is thus inferred that the formation of nanowires of β -Na_xV₂O₅ is due to chemical vapor transport, i.e., following the formation of β -Na_xV₂O₅ due to the reaction of the precursor with the substrate, this material vaporizes. These oxide vapors are transported by the carrier gas in the vicinity of the substrate, leading to the growth of the nanowires when the process was carried at a critical temperature.

4:30 PM U5.10

Morphological Changes while Growing Nickel Monosilicide Nanowires. Joondong Kim¹, Wayne A. Anderson¹, Elena A.

Gulians² and Christopher E. Bunker³; ¹Electrical Engineering, University at Buffalo, Buffalo, New York; ²Energy and Environmental Science Division, University of Dayton Research Institute, Dayton, Ohio; ³Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio.

Nickel monosilicide (NiSi) nanowires (NWs) were fabricated by the Metal Induced Growth (MIG) method and show the morphology changes due to different growth conditions. A n-type Si (100) wafer was coated by Plasma Enhanced Chemical Vapor Deposition (PECVD) to form a 200-300 nm SiO₂ layer as a buffer against Ni diffusion into the Si substrate. Then, Ni was thermally deposited at a thickness of 20-160 nm to serve as a catalyst. This Ni/SiO₂/Si sample was loaded in a DC magnetron sputter system to grow Ni silicide nanowires. The first stage of NW growth starts by forming grooves and agglomeration by thermal heating. Next, the process consists of clustering and fibering stages by interaction of the Ni layer and sputtered Si nanoparticles to control NW growth directions. At times, NWs grew from one fiber to show a segregation phenomenon, which is due to the different thermal expansion rates in Ni silicide and sputtered Si nanoparticles. Scanning Electron Microscopy (SEM) showed the morphology changes of all the sequences. X-ray diffraction (XRD) analysis showed the presence of NiSi peaks as a key factor to grow NWs. Transmission Electron Microscopy (TEM) revealed the single NW to be a single crystal structure and Energy Dispersive spectroscopy (EDS) confirmed the NiSi composition. The NWs have diameters of 20-100 nm, length of 1-10 μ m and surface coverage of 35/10⁻¹² m². Photoluminescence (PL) data indicate an energy gap of 1.7-1.8 eV from a wavelength-independent peak at 675 nm. A clear NW-signal was also observed at 200 cm⁻¹ by Raman spectroscopy. The NiSi NW as a 1 dimensional nanoscale building block has several advantages; low resistivity, little Si consumption and low formation temperature which allows the use of the NiSi NWs as interconnection materials in nanoscale electronics.

4:45 PM U5.11

Surface Diffusion Barriers and Nanostructures Design.

Jian Wang¹, Hanchen Huang¹ and Timothy S. Cale²; ¹Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York.

This paper reports a molecular static study of Cu surface diffusion barriers, particularly the facet-facet and step-facet barriers. The study focuses on two high symmetry surfaces or facets, Cu{111} and

Cu{100}. Our results show that these two barriers are distinct from conventional step barriers and are independent of facet size once it is beyond three atomic layers. Usually, the facet-facet barrier is substantially larger than diffusion barriers on flat surfaces or down monolayer steps, and the step-facet barrier is substantially larger than diffusion barriers along or across monolayer steps. Exceptions do exist. When two Cu{100} facets are involved, the two barriers decrease as the size of the ending facet increases from one layer to two layers, and then increase from two to three (or more) layers. As a result of the large facet-facet and step-facet barriers, surfaces of Cu thin films are on the order of 100 nm. The small facet-facet and step-facet barriers between two Cu{100} facets, when the ending facet is two to three layers, make it difficult to form another Cu{100} facet near one Cu{100} facet. For the same reason, nanowires along $\langle 100 \rangle / \{100\}$ on the Cu{100} is unlikely while nanowires along $\langle 110 \rangle / \{111\}$ are feasible.

SESSION U6: Thermodynamics, Multilayers, and
Microstructure I

Chairs: Peter Anderson and Ruth Schwaiger
Wednesday Morning, December 1, 2004
Room 210 (Hynes)

8:30 AM U6.1

Coupling Between Interfacial Reactions and Stress Evolution in Sn-Cu Thin Film Systems. Lucine Kabakian, Eric Chason and Sharvan Kumar; Engineering, Brown University, Providence, Rhode Island.

When dissimilar materials are brought in contact with each other, interfacial reactions between them can create new compounds and generate stress. Such reactions occur in a number of technologically important processes such as surface treatments and coatings, high-temperature corrosion, diffusion bonding and thin-film contact technology. It is important to understand the evolution of stress in the individual layers, since it may lead to a degradation of electrical and mechanical surface properties. However, the kinetics of stress evolution are complex, depending on a number of factors including the kinetics of interdiffusion and intermetallic compound formation. In this presentation, we will focus on our studies of stress and microstructure evolution in the Sn-Cu system. By using vapor-deposited thin films of Sn and Cu, we can monitor the stress evolution in real time using wafer-curvature based techniques. Our results indicate that the stress evolution in the composite bimetallic films is due primarily to the simultaneous development of tensile stress in the Cu layer and compressive stress in the Sn layer. This is proposed to be a consequence of two simultaneous processes: (1) diffusion of Cu into Sn and subsequent vacancy generation due to the departure of Cu atoms, and (2) formation of Cu_6Sn_5 leading to the creation of excess Sn atoms in the Sn layer. Additional wafer-curvature experiments coupled with XRD stress measurement are used to determine the stress in the Sn layer alone, which appears to provide the driving force for surface relief phenomena such as Sn whisker growth.

8:45 AM U6.2

Self-hardening of nanocrystalline Ti-B-N thin films.

Paul Heinz Mayrhofer and Christian Mitterer; Physical Metallurgy and Materials Testing, University of Leoben, Leoben, Austria.

Nanocrystalline hard films have attracted increasing interest in modern development of hard thin films. Whereas for single-phase thin films a remarkable reduction in hardness occurs around 500°C, nanocomposites may be stable up to 1000°C. In physical vapor deposited Ti-B-N films the nanostructure arises during growth by segregation driven renucleation of TiN and TiB₂ nanocrystals of about 3 nm in diameter. As-deposited films show a hardness of 42 GPa which increases to about 52 GPa during thermal annealing in vacuum. By HRTEM and SAED investigations it was found that as-deposited films have a remarkable amorphous fraction surrounding TiN and TiB₂ nanocrystals. Thermal annealing causes a reduction of the amorphous fraction leading to better-defined nanostructure and interfaces. These processes are responsible for the pronounced hardness increase of such thin films during a thermal treatment. All these mechanisms initiate microstructural changes in the thin films, where the related changes in total free energy can be detected by differential scanning calorimetry. The results obtained show that properties of hard thin films can be designed by their nanostructure, where not only superior properties can be achieved. They have also the potential of a tailored response and even improvement of their properties during high-temperature applications.

9:00 AM U6.3

Stability of Nanoscale Twins in Sputtered 330 Stainless Steel Thin Films. Xinghang Zhang, Amit Misra, Haiyan Wang and

Richard G. Hoagland; Mater. Sci. Tech. Div., Los Alamos National Laboratory, Los Alamos, New Mexico.

We have recently discovered that sputter-deposited austenitic 330 stainless steel (330 SS) thin films have a nanoscale twinned structure. These twins are of {111} type with an average twin spacing of a few nanometers and the twin planes have a preferred orientation normal to the growth direction. The as-sputtered films have hardness values approaching 7 GPa, about an order of magnitude higher than bulk 330 SS. This unusually high strength originates from the high resistance of twin interfaces to slip transmission, as revealed by molecular dynamics simulations. In this paper we report on the thermal stability of these nanoscale twins. The evolution of mechanical behavior and electrical transport properties during annealing are correlated to the variation of microstructure such as the average twin spacing and columnar grain sizes. In addition, we explore the effect of residual stress on the formation of nanoscale twins in 330 SS.

9:15 AM U6.4

Thermal stability of nanocrystalline Ni-Fe alloys.

Fereshteh Ebrahimi and Hongqi Li; Materials Science and Engineering, University of Florida, Gainesville, Florida.

One of the limitations of nanostructures is their instability at elevated temperatures. One method to improve the thermal stability of nanocrystalline metals is by slowing down the grain boundary migration via solute drag. In this study, nanocrystalline Ni-15%Fe and Ni-21%Fe alloys were produced by the electrodeposition technique and their thermal stability was evaluated as functions of temperature and time. The structure of the alloys was characterized using XRD (x-ray diffraction) and TEM (transmission electron microscopy). The results of this study confirm that the addition of iron increases the thermal stability of nickel. However, the isothermal annealing shows that the time exponent is comparable to that of pure nickel, suggesting that the mechanism of grain growth is similar. The Arrhenius type analysis of the grain growth in the Ni-Fe alloys revealed two distinct temperature regimes, where at low temperatures the grain boundary diffusion is prominent, while at high temperatures the lattice diffusion takes over. In this presentation the changes in the structure of nanocrystalline Ni-Fe alloys with isothermal and isochronal annealing are discussed.

10:00 AM *U6.5

Dynamic Grain Growth in Fine Grained Metals.

Cynthia A. Volkert¹, R. Monig¹, Y. B. Park², R. Schwaiger¹ and E.

Rabkin³; ¹Forschungszentrum Karlsruhe, Institute for Materials Research II, Karlsruhe, Germany; ²Andong National University, Andong, South Korea; ³Technion, Haifa, Israel.

Recent observations show that deformation during straining can significantly enhance grain growth in thin metal films and other fine-grained metals. This microstructural instability, which was previously believed to be limited to superplastic materials, poses a threat to the use of fine-grained materials in many applications. Dynamic grain growth has been observed during both monotonic and cyclic loading of fine-grained metals and can lead to homogeneous microstructural coarsening and to abnormal growth of individual grains. An increase in grain size by as much as a factor of 20 has been observed and is most apparent in materials with a very fine initial grain size. In this talk, the experimental observations of dynamic grain growth during deformation of non-superplastic thin film and nanocrystalline metals will be reviewed. A number of possible mechanisms for the phenomenon will be discussed including depinning of grain boundaries by dislocation pile-ups and increased grain boundary diffusivity by deformation-generated defects. The implications of dynamic grain growth on microstructural evolution during heating of thin films on substrates and on microstructural stability in the limit of very small grain sizes will also be addressed.

10:30 AM U6.6

In-Situ TEM Observation of Grain Growth of Nanograined Thin Films. Khalid Mikhil Hattar¹, Jong Hee Han², Jennifer Ann

Gregg¹, Taher A. Saif² and Ian M. Robertson¹; ¹Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois; ²Mechanical and Industrial Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois.

In-situ transmission electron microscopy (TEM) analysis is used to study the stability of nanograined and ultra-fine grained thin films at elevated temperature. Grain growth has been observed in both free-standing and constrained nanograined gold and copper thin films. The formation and destruction of twins was observed to play a critical role in the grain growth rate, with the twins retarding the growth rate. These dynamic observations of grain growth will be compared to computer simulation results and to current theory.

10:45 AM U6.7

Morphological Evolution and Stabilization of Nanoporous Gold and Pt-Coated Nanoporous Gold. Yi Ding, Anant Mathur, Young-Ju Kim and Jonah Erlebacher; Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

Nanoporous gold is an open bicontinuous mesoporous metal made by selective etching of silver from silver/gold alloys. During etching, gold atoms diffuse along the alloy/electrolyte interface and reconfigure themselves into the porous network. Because this interfacial diffusion is confined to the original crystal lattice of the original alloy, the final material has the same grain size distribution as the starting material. Average pore sizes in this material may be made with dimensions less than 10 nm, typically less than 3 orders of magnitude smaller than the grain size. For this reason, nanoporous gold provides a unique three-dimensional morphology with which to probe the stability of porous nanostructures without complications associated with multiple-components and grain-boundaries. In this study, we present our work on the morphological evolution of nanoporous gold in a number of different chemical environments and electrochemical potentials, and will also show how to stabilize the nanoscale morphology against thermal coarsening by coating porous gold with an ultra-thin skin of platinum.

11:00 AM U6.8

Thermomechanical Behavior and Microstructure Evolution in Tantalum Thin Films. Robert Knepper, Katherine Jackson and Shefford P. Baker; Materials Science and Engineering, Cornell University, Ithaca, New York.

Tantalum thin films are used in a number of microelectronic and x-ray optics applications. Stresses that build up in these films during thermal cycling can cause reliability problems in devices. Sputter-deposited tantalum thin films are often prepared so as to have a metastable tetragonal crystal structure (β phase). Such films may undergo changes in stress on the order of several GPa in the tensile direction if the film transforms to the stable bcc structure (α phase) during thermal cycling. The origin of these enormous stress changes is not known, as there has been little study of the phase-transformed microstructure. β -Ta films prepared in an ultra-high vacuum sputter deposition system were thermally cycled to 750° C. Stresses were measured during cycling, using an in situ substrate curvature measurement system. The phase transformation from β to α takes place in conjunction with distinct jumps in stress in the tensile direction at approximately 400° and 650° C. X-ray and electron backscattered diffraction (EBSD) analyses are used to determine grain sizes, along with crystal phase and orientation information. The results indicate a significant amount grain growth accompanying the phase transformation, contributing to the observed stress change. It is found that the measured total stress change is in reasonable agreement with that predicted by the combination of grain growth and densification processes associated with the phase transformation.

11:15 AM U6.9

The Structure and Stability of β -Ta: A Experimental and Theoretical Study. Aiqin Jiang¹, Trevor A. Tyson¹ and Lisa Axe²;

¹Physics Department, New Jersey Institute of Technology, Newark, New Jersey; ²Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, New Jersey.

Tantalum thin films exhibit two crystalline phases, bcc (α -phase, the bulk structure of tantalum) and metastable tetragonal β -phase, which differ in both mechanical and electrical properties. In order to understand the origin and stability of the β phase, β -Ta films, deposited by magnetron sputtering on different substrates, have been studied using x-ray diffraction measurements and molecular dynamics simulations performed on tantalum clusters. The same space group is formed by deposition of films on a broad range of substrates with varying experimental conditions. Molecular dynamics simulations show that the phase is stable with a very high melting point. No phase transformation was observed for pure β -Ta clusters. Simulations of Ta clusters with mixed α and β phases revealed that inclusion of a small α -Ta cluster within a β -Ta cluster induces transformation to bcc at a temperature far below its melting point, depending on the cluster size and α to β ratio. These results suggest that the observed transformation results from the presence of small α -phase grains within the β -Ta films.

11:30 AM U6.10

Molecular Dynamics Study of the Prevention of Grain Growth in Nanocrystalline Materials by Use of Doping.

Paul Christopher Millett¹, R. Panner Selvam¹ and Ashok Saxena²;

¹Civil Engineering, University of Arkansas, Fayetteville, Arkansas; ²Mechanical Engineering, University of Arkansas, Fayetteville, Arkansas.

In recent years, nanostructured materials (NSMs) with grain sizes in the submicron range (3-100 nm) have received much interest because they exhibit several attractive properties compared to coarse-grained polycrystals of the same material. Unfortunately, due to the high density of grain boundaries present in NSMs, which translates into high grain boundary energies (E_{GB}), the microstructure is quite unstable at even low temperatures resulting in rapid grain growth. In order for the novel mechanical, magnetic, and electrical properties of NSMs to be realized in real-world applications, it is necessary to determine methods for maintaining the grain size in the nanometer range. It has been theoretically predicted that, for alloy systems with a large heat of segregation, the nanocrystalline alloy is in a metastable state for a particular grain size which decreases with increasing concentration of solute element. That is to say that if the Gibb's free energy of a polycrystalline alloy is below that of the single crystal solid solution, the driving force for grain growth has been eliminated. However, this theoretical conjecture has yet to be achieved in experimental efforts. In this paper, molecular dynamics (MD) have been used to simulate a virtual nanocrystalline alloy sample with solute atoms segregated to grain boundaries between pure solvent crystallites. MD is an effective tool for this study because the total E_{GB} can be measured before temperature is introduced. The atomic radii and concentration of solute atoms as well as the initial grain size have been varied to determine how to most effectively prevent grain growth at elevated temperatures. A nonuniform distribution of solute atoms throughout the sample has also been arranged to study if uneven grain growth can occur even if the total E_{GB} is less than or equal to zero. In addition to the temperature effects, tensile tests are performed to determine if the presence of the solute element at grain boundary segregation sites may reduce the strength or ductility of the nanocrystals.

11:45 AM U6.11

Stability of Ultrathin Surface Oxides on Silicon. Ana Ramos¹, Ming Tang¹, Sung-Yoon Chung², Yet-Ming Chiang¹, W. Craig Carter¹ and M. Gautier-Soyer³; ¹Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²School of Materials Science and Engineering, Inha University, Incheon, South Korea; ³DSM/DRECAM/SPCSI, CEA Saclay, Gif sur Yvette, Cedex, France.

Interfacial oxide films are critical components in current silicon microelectronics (i.e., as gate oxides), and likely to be equally important in future nanoelectronic devices. Intergranular and surface oxide films of *thermodynamically* controlled thickness (1 nm) are known to form in materials such as doped silicon nitride, silicon carbide, and zinc oxide. The goal of this work is to determine whether similar phenomena can be exploited to produce stable ultrathin surficial oxides on silicon. Taking oxygen to be the primary impurity/adsorbate, the ambient oxygen activity was systematically controlled at low levels in the vicinity of bulk Si/SiO₂ equilibrium. This was accomplished by annealing silicon {001} wafers in the presence of metal/metal-oxide buffers, e.g., Zr/ZrO₂, in sealed systems at temperatures of 700-1100C. Angle-resolved XPS measurements were then performed to determine the thickness and stoichiometry of the films. For purely siliceous films, it was found that a stable nanometer-thick film forms at oxygen activities slightly above the saturation value corresponding to bulk Si/SiO₂ equilibrium. The effect of the buffer system and temperature on film thickness and stability, and the implications of this work for the processing and properties of alternative gate oxide materials, will be discussed.

SESSION U7: Thermodynamics, Multilayers, and Microstructure II

Chairs: Richard Vinci and Cynthia Volkert

Wednesday Afternoon, December 1, 2004

Room 210 (Hynes)

1:30 PM U7.1

Stability of Immiscible Binary Metallic Multilayered Systems:

A Thermodynamic Criterion on the Nanoscale. L. H. Liang^{1,2}, Hong-Jun Gao¹, Cheng-Xin Wang² and Guo-Wei Yang²; ¹Institute of

Physics, Chinese Academy of Sciences, Beijing, China; ²State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics Science & Engineering, Zhongshan University, Guangzhou, China.

Layered structures are found in a number of applications ranging from magnetic to structural, and the stability of the individual layers is often critical to the performance of the material. Especially, stable layered microstructures are important in many low to moderate temperature applications, such as multilayered devices in magnetic storage and copper lines in integrated circuits, because the layers must resist coarsening and breakdown, which is driven thermodynamically by free energy of the interfaces. Therefore, understanding the thermodynamic driving forces that degrade the

layering in multilayers is of major technological importance. Basically, the thermodynamic driving force in multilayers to destroy the layering includes chemical energy, elastic strain energy, and interface free energy. However, for immiscible binary metallic systems, multilayers are chemically stable due to their positive heat of mixing. In this case, we pay attention to the stability of immiscible binary multilayers under the thermodynamic driving force just including elastic strain energy and interface free energy. Thermodynamically, the stability of immiscible binary metallic multilayered systems mainly depends on the balance between the thermodynamic driving force and the positive heat of mixing. The drive leads to instabilities in the layered structure through interface mixing such as alloying when the thermodynamic forces are larger than the positive heat of mixing. Since the starting point of the instability is usually limited in the interface section (a few nanometers), an analytic thermodynamic criterion for the stability of multilayers on the nanoscale is pursued in this study. Based on two terms, the main chemical term related with interface energy of nanocrystals with pure element and the additional structure term induced by mismatch and dislocation strain energies due to different elements, an analytic thermodynamic model at the nanometer scale, without adjustable parameter, is developed to calculate the size-dependent interface energy and mixing heat of binary metallic multilayered systems. The theoretical results are in well agreed with the theoretical calculations of embedded atom method and molecular dynamic simulation. Furthermore, based on this model, a nanosize-dependent thermodynamic criterion of for the stability is proposed to elucidate interface alloying in immiscible binary metallic multilayered systems. Notably, the theoretical predictions are good consistent with experimental data. Consequently, we expect the nano-scaled thermodynamic approach to be a general approach to explore the stability in binary systems.

1:45 PM U7.2

Surface Instability of a Nano-scale Multilayer Thin Film System. Yueguang Wei, Di Jiang and Ajing Cao; Institute of Mechanics, Chinese Academy of Sciences, Beijing, Beijing, China.

The nano-scale multilayer thin film system, with its unique characteristics, has closely connected with most advanced nano-materials, and has been widely applied to the MEMS area and the surface- and interfacial-engineering areas. Its fundamental roles played in the micro-systems and in the modern materials are not only as protection layers or connection layers between device with device, but also as the strengthening or the toughening of material, etc. The main failure form of the nano-scale multilayer thin film system usually is surface instability due to mismatch compressive residual stress within the surface layer. The surface kink bands and damage bands are formed near the material surface. Additionally, some kinds of failure patterns appear on the material surface due to thin film delamination. In order to investigate the failure mechanism, in the present research, a theoretical model based on the Hill-Hutchinson's surface instability theory is presented and developed. Motivated by continuum damage analysis, the surface instability process for the nano-scale multilayer thin film system is formulated through homogenizing a set of field equations and bifurcation analysis. The surface failure patterns, such as the "surface islands" microstructures, etc., are modeled and computed through bifurcation and post-bifurcation analysis. Moreover, in the present research, the atomic force microscopy (AFM) observation and measurement for a nano-scale multilayer film system of copper will be performed, and the comparison of theoretical modeling with microscopic observation and measurement are carried out and discussed.

2:00 PM *U7.3

Controlling Stability in Multilayer Foils for Experimental Investigations and Commercial Applications. Timothy P. Weisb,

¹Department of MS&E, Johns Hopkins University, Baltimore, Maryland; ²Reactive NanoTechnologies, Inc., Hunt Valley, Maryland.

The first half of this presentation explores the microstructural stability of immiscible A/B microlaminate samples and their use as model materials for studying creep deformation in fine-grained sample. Through a careful choice of materials systems, one can produce samples with micro-scale layers and grain structures that are chemically and physically stable during high temperature testing. In addition, standard, bulk tension techniques can be used to test these microlaminate samples because total thicknesses can range from 20 to 200 μ m, even though the individual layers in the laminates are just micrometers thick. After reviewing the stability of several A/B immiscible systems, the time dependent deformation of fine-grained Nb will be described, based on creep tests of Cu/Nb microlaminates at 600°C. The second half of this presentation will focus on the chemical stability of miscible A/B nanolaminates that are now used as local heat sources for soldering and brazing. These nanolaminates consist of thousands of alternating nanoscale layers that mix exothermically and can yield a self-propagating reaction once the mixing is initiated. After describing their application as local heat sources, the

presentation will focus on predicting, measuring, and controlling the power density that is required to initiate the self-propagating reactions in Ni/Al foils. Initiation requirements are predicted using numerical models of atomic and thermal diffusion, they are measured using pulses of electrical energy and they are controlled by varying nanolaminate geometries such as individual layer thickness and intermixing between the individual layers.

2:30 PM U7.4

Thermal Grooving in Multilayer Thin Films: The Effect of Microstructural Scale. Peter M. Anderson¹, Jue Wang¹ and Sridhar Narayanaswami²; ¹Materials Science and Engineering, Ohio State University, Columbus, Ohio; ²Rockwell Science Center, Thousand Oaks, California.

Multilayer thin films, when heated, can undergo a grooving instability whereby layers having a columnar grain structure pinch off along the numerous grain boundaries that traverse the film. This presentation advances the classic Mullins treatment of thermal grooving by considering a multilayer thin film that is heated and also strained via in-plane biaxial tensile loading. The analysis extends the Thouless framework and method of solution for single films to a 2D multilayer geometry having a columnar grain structure. A primary question posed is whether multilayer thin films are expected to become more unstable to thermal grooving as bilayer thickness is decreased. The results suggest that there is a critical grain aspect ratio, dependent on grain boundary and interfacial energies, above which multilayer thin films are stable to pinch off, regardless of the bilayer thickness. In this regime, the film layers acquire a stable zig-zag structure. Below this critical aspect ratio, the time to pinch-off is proportional to (layer thickness)⁴. Thus, decreases in layer thickness can have a catastrophic effect on thin film stability. An added effect in many systems is the transition from semi-coherent to coherent interfacial structure with decreasing layer thickness. This feature decreases the stability of nano-scale multilayer thin films by shifting the critical grain aspect ratio. The resulting features of this diffusional analysis will be compared to experimental observations of grooving in metallic and intermetallic multilayer thin films.

2:45 PM U7.5

Morphology and Microstructure Evolution of Multilayer Au/Cr/Si Thin Films Subject to Annealing. David Miller^{1,2}, Nancy Yang², Cari Herrmann^{1,3}, Hans Maier⁴, Steve George³, Conrad Stoldt¹ and Ken Gall¹; ¹Mechanical Engineering, University of Colorado, Boulder, Colorado; ²Analytical Materials Science Group, Sandia National Laboratories, Livermore, California; ³Chemistry & Biochemistry, University of Colorado, Boulder, Colorado; ⁴Lehrstuhl for Werkstoffkunde, University of Paderborn, Paderborn, Germany.

Au/Cr/Si devices find use in optics, electronics, chemical & biological sensing, micro-actuation, as well as fabrication process monitoring applications. Behavior in these multilayer devices differs from that in traditional thin films studies owing to the comparable thicknesses of the various layers and the resulting difference in stress distributions. Also, the metallic layer is studied in its as-deposited state as necessitated by microsystem applications. Arrays of Au/Cr/Si microcantilevers subject to isothermal hold conditions exhibit dimensional instability as a function of time measured through change in curvature. We have performed characterization in the temperature range of 50 to 225 deg C and we observe, for example, drastic and non-intuitive changes in curvature for specimens annealed in air at 225 deg C for less than 24 hours. The changes observed will influence design performance as well as device reliability. To understand the cause of observed thermomechanical behavior, we focus here on the evolution of the gold's microstructure and surface morphology to identify operant mechanisms. Cross-sectional TEM evidenced an initial tapered columnar microstructure containing twins and dislocations, which evolved upon annealing. Variation in defect density suggests non-uniformity in stress distribution within the grains and at the substrate interface. FE-SEM imaging revealed prominent grain boundary grooving. Electron Backscatter Diffraction Pattern (EBSP) mapping of the as-deposited gold possesses strong {111} texture normal to the film's surface. After annealing the gold still possesses {111} texture, with a minor {001} component. EDX analysis of the TEM foil specimens showed an increase in chromium concentration at the free surface of the gold possibly facilitated by diffusion of the original chrome layer. To gain further understanding of microstructure evolution and atomic diffusion, we deposited various nano-scale alumina coatings using the atomic layer deposition (ALD) technique. Alumina was found to stabilize the thermomechanical behavior and also alter the evolution of the film's surface morphology and its chemical composition. It is postulated that when coatings of sufficient thickness are used, the alumina may prevent the oxidation of chrome at the free surface of the gold, decreasing the driving forces responsible for mass transport and ultimately improving the stability of the Au. Operant mechanisms will be discussed in greater detail in the full paper and presentation.

SESSION U8: Poster Session: Microstructure,
Processing and Properties
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

U8.1
Density Changes and Viscous Flows during Structural Relaxation of Plasma-Enhanced Chemical Vapor Deposited Silicon Oxide Films. Zhiqiang Cao and Xin Zhang; Manufacturing Engineering, Boston University, Brookline, Massachusetts.

Plasma-enhanced chemical vapor deposited (PECVD) silane-based oxides (SiO_x) have been widely used in both microelectronics and MEMS (MicroElectroMechanical Systems) to form electrical and/or mechanical components. During fabrication of such microelectric and MEMS devices, PECVD SiO_x undergo many thermal cycles, which often causes unwanted changes in thermal-mechanical properties of the material, and consequent degradation of device performance and reliability. As an extreme example, recent developments in Power MEMS (micro power-generation devices) require thick (15-40 microns) PECVD SiO_x as insulation layer. However, stresses generated during deposition and subsequent thermal cycling often cause significant wafer bow or even cracks which deteriorate the integrity of such MEMS structures. This paper discusses the thermal-mechanical response of PECVD SiO_x during deposition and subsequent thermal cycling. A series of in-situ wafer-curvature based stress measurement experiments of up to 500°C were conducted for PECVD SiO_x films of various thicknesses ranging from below 10 microns to 10s of microns. Annealing effects were also investigated with peak temperature of up to 1100 °C. Non-thermal, tensile stresses were observed during deposition and significant hysteresis was observed during the first thermal cycling. During subsequent thermal cycling's, however, such hysteresis was generally much reduced. After high temperature annealing at 1100 °C, the hysteresis effect vanished but the stress became more compressive. Two factors, density change and plastic deformation, were identified as controlling mechanisms of stress changes in the films. A quantitative case-study of both density change and viscous flow has been done based upon experimental results. It was found that for 10 microns thick PECVD SiO_x film under 500°C thermal cycling, the density decreased about 0.3% at peak temperature. Plastic flows with different viscosities and amplitudes were observed during annealing at 500°C. The viscosities of the waves with two most significant amplitudes have a viscosity of 1.8e13Ns/m² and 9.2e13Ns/m², respectively. A microstructure based mechanism relates defects during PECVD deposition to both density change and viscous flow. This mechanism elucidates "seams" as source of density change and "voids" as source of plastic deformation, accompanied by viscous flow. This mechanism was then applied to explain other experimental results of thermal cycling as well as annealing of PECVD SiO_x films, including stress hysteresis generation and reduction, and coefficient of thermal expansion (CTE) changes.

U8.2 TRANSFERRED TO U10.11

U8.3
An Adhesion Study of Amorphous Silicon Thin Films: The Effects of Hydrogen Diffusion. Youbo Lin and Joost Vlassak; DEAS, Harvard University, Cambridge, Massachusetts.

Hydrogenated amorphous silicon (a-Si:H) is an important material used in modern flat panel displays, as well as for micro- and opto-electronic devices thanks to its great electrophysical properties. The energetics, transport, and kinetic behavior of hydrogen in silicon and in hydrogenated amorphous Si in particular have been widely investigated. The effect of hydrogen diffusion on the mechanical stability of amorphous Si films at the elevated temperatures often encountered during fabrication processes, however, is still open for discussion. It has been found that hydrogen blisters form at the interface between two amorphous silicon thin films. The evolution of these hydrogen blisters at elevated temperature was investigated using optical and atomic force microscopy in combination with rapid thermal anneals. It is found that the hydrogen pressure in the blisters and the residual stress in the Si films provide the driving force for blister growth. A fracture-mechanics based model that incorporates hydrogen diffusion will be proposed to describe the behavior of these hydrogen blisters and the stability of the amorphous silicon thin films.

U8.4
Trapping of hydrogen in carbon nitride films during or after high temperature heat treatment. David C. Ingram¹, Asghar Kayani¹, William C. Lanter² and Charles A. DeJoseph³; ¹Physics and Astronomy, Ohio University, Athens, Ohio; ²Innovative Scientific Solutions, Corp., Beavercreek, Ohio; ³Air Force Research Laboratory

Thin films of carbon nitride deposited by ion beam assisted deposition or magnetron sputter deposition typically contain a significant fraction of hydrogen, 1-30 atomic % (at.%). In order to improve the thermal stability of the properties the films, attempts have been made to reduce the hydrogen trapped during deposition to a minimum. Such films typically have less than 5 at.% hydrogen. On heating these films in ultra high purity (99.999%) argon, it has been found that above 600° C the films start to absorb hydrogen up to 60 at.%. This is determined using Rutherford Backscattering Spectroscopy in combination with Elastic Recoil Spectroscopy. In this paper the possible sources of the hydrogen will be investigated by various techniques, including the use of deuterated isotopic labeling of possible sources of hydrogen.

U8.5
Abstract Withdrawn

U8.6
Stable Intergranular Films in Silicon Nitride from a Phase-Field Model. Catherine M. Bishop^{1,2}, W. Craig Carter² and Rowland M. Cannon³; ¹Department of Materials, Oxford University, Oxford, United Kingdom; ²Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; ³Lawrence Berkeley National Laboratory, Berkeley, California.

Silicon nitride is one ceramic that has stable intergranular films. These films are an interface stabilized second phase with spatially varying structure and chemistry. The first models to explain this stability neglected the coupling between structure and chemistry. A general phase-field model that couples chemistry, structure, and electrostatics will be presented. The binary simplification for the silicon dioxide-silicon nitride system is analyzed for the conditions that produce stable intergranular films. These conditions exist at chemical potentials corresponding to bulk solid silicon nitride both above and below the eutectic. The coupling that produces this effect and comparisons to experimental data will be discussed.

U8.7
Stability of WC_x Nanoparticles for NO_x Reduction. S. Ismat Shah¹, Abdul Rumaiz², Jinguang G. Chen⁴ and Minghui Zhang³; ¹Materials Science and Physics, University of Delaware, Newark, Delaware; ²Physics and Astronomy, University of Delaware, Newark, Delaware; ³Materials Science and Engineering, University of Delaware, Newark, Delaware; ⁴Chemical Engineering, University of Delaware, Newark, Delaware.

WC_x nanoparticles were synthesized using various Physical Vapor Deposition (PVD) methods such as reactive sputtering and Pulsed Laser Deposition (PLD). In both the methods the metal flux obtained is condensed in the presence of He gas. The structural properties of the samples were investigated using X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The feasibility of using nano WC_x as an alternative catalyst for Pt will also be addressed. The synthesized WC_x were used to check for the reduction of NO_x in a simple reactor. Nano WC_x shows activity at temperatures starting from 400°C, the sample also showed no structural change before and after the experiment showing that WC_x is not getting oxidized from the reaction. The stability of nano WC_x was studied by performing the same experiment at a fixed temperature (where the activity is appreciable) for an extended period of time. For comparison the similar experiment was done with Pt coated on γ Alumina. This sample showed higher activity at lower temperature when compared with nano WC_x. Various aspects of improving the efficiency of nano WC_x will be presented.

U8.8
Nucleation and growth phenomena in the evolution of metal silicide thin films. Ramanathan Krishnamurthy^{2,1} and David J. Srolovitz^{2,1}; ¹Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey; ²Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey.

The effects of stress and microstructure (grain boundaries, surfaces and interfaces) on the thermodynamics and kinetics of solid state transformations attain heightened importance in thin film systems. In this work, we present a thermodynamic analysis of nucleation and growth energetics in thin film systems. Nucleation at grain boundaries, film free surface, interfaces and triple junctions are naturally considered in this analysis. Results for the energetically favored size and shape of the nuclei at several locations within the thin film system are presented. These results are critically analyzed with regard to the effects of stress and the film free surface on the shape and size distribution of the energetically favorable nuclei. The results are compared to experimental NiSi film results and the implications of

these results for CMOS device applications will be discussed. The role of silicide faceting on nucleation and growth kinetics will also be considered.

US.9

Shape and Stability of TiO₂ Nanoparticles in Water: Why the Wulff Construction is Not Enough. Amanda S. Barnard^{1,2}, Peter Zapol^{1,2,3} and Larry A. Curtiss^{2,3}, ¹Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

The potential of titanium dioxide nanoparticles for advanced photochemical applications has prompted a number of studies to analyze the size, phase and morphology dependent properties. Previously we have used a thermodynamic model designed to describe nanoparticles as a function of size and shape to investigate the effects of shape on the size dependence of the relative stability of the anatase to rutile phases. This work has now been extended to consider titanium dioxide nanoparticles in water, so as to examine the effects of adsorption on the equilibrium shape and the phase stability. Density functional calculations have been used to accurately determine surface energies and surface tension of low index hydrated stoichiometric surfaces of anatase and rutile for various adsorption configurations, while the thermodynamic model has been used to optimize the nanoparticle shape as a function of size. The results illustrate that the phase transition size varies with shape and chemical environment, and highlights how the Wulff construction is insufficient for describing morphology at the nanoscale. This work has been supported by the U.S. Department of Energy BES-Chemical Sciences, under Contract W-31-109-ENG-38.

US.10

Environmental Effects on the Structure and Properties of Yttria-Stabilized Zirconia Thin Films. Jeffrey Robert Piascik^{2,1}, Christopher A. Bower¹, Brian R. Stoner^{1,2} and Jeffrey Y. Thompson^{3,2}; ¹Materials and Electronic Technologies Division, MCNC-Research and Development Institute, RTP, North Carolina; ²Curriculum of Applied and Materials Science, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina; ³Department of Operative Dentistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

Zirconia is a material that possesses a unique set of material properties. Due to its high toughness, excellent wear properties, and thermal stability, zirconia thin films can be used for a variety of applications ranging from biomedical to thermal barriers. The objective of this research is to study environmental effects on the mechanical properties of such films. Yttria (3 mol%)-stabilized zirconia (YSZ) thin films were deposited using radio frequency (RF) magnetron sputtering. The YSZ thin films were deposited over a range of temperature (22 - 300°C), pressure (5 - 25 mTorr), and background oxygen levels (0 - 6 sccm). Initial studies characterized a select set of properties in relation to deposition parameters including: refractive index (prism coupler), structure (XRD), stoichiometry (RBS), and residual stress (wafer curvature). X-Ray Diffraction (XRD) showed that the films are comprised of mainly monoclinic and tetragonal crystal phases. The film refractive index determined by prism coupling, depends strongly on the deposition conditions and ranged from 1.960 to 2.247. Wafer bow measurements indicate that the sputtered YSZ films can have initial stress ranging from 100 MPa tensile to 300 MPa compressive, depending on the deposition parameters. Exposure to ambient conditions (25°C, 1 atm, 75% humidity), which over a period of 30 days shifted the measured residual stress in the compressive direction. Samples were then heated in vacuum (100°C, 12 hr, 10⁻⁷ Torr) and stress values were re-measured as a function of time. This environmental cycling allowed compressive stresses to be related to water vapor adsorption/absorption and evaporation. These effects were then evaluated for films, constructed under different deposition parameters, of varying density and crystal structure. Several models will be discussed describing the incorporation of water vapor into the film structure. Results of mechanical tests can then be discussed in relation to environmental effects. This work is supported through NIH-NIDCR R01 DE013511.

US.11

Improving the Adhesion Properties of Nanocrystalline Diamond Films by Bias-Enhanced Nucleation. Ericka Mujica¹, Scott Wolter², Fabrice Piazza¹ and Gerardo Morell³; ¹Dept of Physics, University of Puerto Rico, San Juan, Puerto Rico; ²Materials Science & Engineering, North Carolina State University, Raleigh, North Carolina; ³Dept of Physical Sciences, University of Puerto Rico, San Juan, PR, Puerto Rico.

Nanocrystalline diamond films (including materials referred to as tetrahedrally-bonded carbon films, ultra-nanocrystalline diamond

films, and nanostructured diamond films) are highly strained materials that show a strong tendency to delaminate at relatively small thickness values around 5 microns. This situation often precludes from taking advantage of the many extreme properties of diamond that make it suitable for protective and tribological coatings (i.e. extreme hardness, radiation hardness, chemical inertness). We have employed bias-enhanced nucleation (BEN) performed in a microwave-plasma chemical vapor deposition (MWCVD) system to implant seed nanostructures in the substrate that favor the formation of strongly adherent layer at the substrate-film interface. Nanocrystalline diamond films are deposited on the BEN substrates using a hot-filament chemical vapor deposition (HFCVD) system in the continuous secondary nucleation mode that results in the deposition of nanocrystalline diamond. The observed changes in the film nanostructure indicates the controlling role that seeding has on film evolution. Although the films remain highly strained at the nanoscale, as evidenced from the Raman spectra, they can be grown to large thickness values without compromising the substrate adhesion. Thermal shock tests evidenced the ability of these films to differentially expand and contract while remaining firmly attached to the substrate. These results are discussed in terms of the formation of a thin strong disordered carbide buffer layer at the substrate-film interface capable to adjust and accommodate dynamically any lattice mismatch. The formation of this thin carbide layer is strongly enhanced by the application of BEN to the substrates. 1. S.D. Wolter, F. Okuzumi, J.T. Prater, and Z. Sitar, AC vs. DC bias-enhanced nucleation of highly oriented diamond on silicon (100), J. Electrochem. Soc., 149, G114-117 (2002). 2. S. Gupta, B.R. Weiner, G. Morell, Synthesis and characterization of sulfur-incorporated microcrystalline diamond and nanocrystalline carbon thin films by hot filament chemical vapor deposition, Journal of Materials Research 18, 363 (2003).

US.12

Thin Films Stress Aging Study using Micromachined Cantilevers. Christophe Malhaire¹, Alexandru Andrei¹, Sebastiano Brida² and Daniel Barbier¹; ¹LPM, INSA, Villeurbanne, France; ²Aerospace Division, Esterline Sensors, Bourges, France.

The purpose of the present work was to study the long term stress stability of thin films used in harsh environment sensors. Stress measurements for mono and multilayer dielectric (silicon oxide and nitride) and metal (AlTi and TiW) thin films have been periodically performed at room temperature after thermal aging at 150 C. An improved method for measuring stresses using bulk micromachined Si cantilevers with different lengths is presented. The stress-deflection analytical model has been corrected by means of 3D finite element analysis in order to take into account cantilevers clamping conditions and film on Si thickness ratio. Cantilevers have been achieved on double side polished, 4 inches (100) silicon wafers. Thermal silicon oxide (1.5 μm thick, 1130 C) and LPCVD silicon nitride (0.1 μm, 800 C, 15 min, 0.2 torr, in a silane rich atmosphere) have been used as masking layer. The boundaries of the cantilevers have been defined on the top side by DRIE (20 μm depth using a resist mask). The cantilevers have been released from the substrate by bulk anisotropic etching of the backside using an aqueous KOH solution. The front side has been protected against the etching solution by means of a sample holder and a wax film. Sputtering, without substrate heating, of 0.2 μm thick AlTi (less than 10 wt.% Ti) and 0.1 μm thick TiW (10 wt.% Ti) have been performed on the front side of bare Si cantilevers. Cantilever thickness has been measured using a double side auto focus microscope system (Micro Control THN-500). Their deflection had been measured by optical profilometry (UBM Microfocus). Absolute stress measurements were obtained with only a 15% accuracy due to cantilever thickness uniformity and measurements accuracy. However, stress relative changes have been determined with a 2% accuracy. Stress values for silicon oxide and nitride of -240 MPa and 280 MPa, respectively, are in good agreement with the literature. Stress values for as-deposited AlTi and TiW films were 50 MPa and -800 MPa, respectively. After a standard 450 C / 30 min in a N₂+H₂ atmosphere annealing, stresses have changed to 200 MPa and -720 MPa, respectively. No further change has been observed for TiW after 1 month exposure at 150 C / air. However, a slight 5% stress decrease has been pointed out for AlTi after 2 weeks 150 C / air thermal aging. These results show that TiW, which is generally used as diffusion barrier, has a stable stress state for applications up to 150 C. Stress change in AlTi films may be correlated with Ti oxidation.

US.13

Atmospheric Stability of E-Beam Deposited Optical Thin Films. Ping Hou¹ and Sun Lianchao²; ¹SuperPower Inc., Schenectady, New York; ²Sun International (USA), Acton, Massachusetts.

Thin film technology constructs one of the foundations in manufacturing micro-electro-mechanical systems (MEMS) and semiconductor devices. However, preventing undesirable changes in

mechanical, micro-structural, and optical properties for functional thin films still remains a big challenge. In this study, multi-layer stack with alternating SiO₂-TiO₂ optical thin films at non-quarterwave thickness were prepared by the technology of electron beam (e-beam) evaporation with ion beam assistant deposition (IBAD). The evolution of mechanical (stress) and optical properties of as-deposited thin films were studied as the function of time in the atmospheric environment. It was found that the thin film stress in this experiment becomes more and more compressive after several hundred hours exposition at ambient temperatures. Dehydrating experiment conducted under a high vacuum chamber indicates the existence of water moisture inside the exposed thin films. Annealing experiments at 150C and 250C further reveal the effect of moisture on the mechanical property. It was also found that the spectrum of these naturally exposed optical thin films shifts towards the lower wavelength direction. Theoretical simulations show that such a shift corresponds to the refractive index changes through water absorption. Therefore, it is believed that the absorption of water moisture into the e-beam deposited thin films predominates the changes of stress and optical properties at low atmospheric temperature (<150C). To this end, making a dense film is a practical approach of enhancing stability.

U8.14

Superhydrophobic nanowires springs. Ghim Wei Ho¹, Andrew S. W. Wong², William G. Proud³ and Mark E. Welland¹; ¹Engineering, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom; ²Material Science and Metallurgy, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom; ³Physics, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom.

For years, scientists have sought to replicate the water-beading and self-cleaning properties of the lotus plant and wings of a butterfly. Here we have grown a nanobed with springy and self-cleaning silicon carbide (SiC) nanowires using simple chemical vapor process [1]. It has successfully tailored surface roughness to produce a super-hydrophobic surface with a high contact angle (CA) >170 degree. SiC nanowires have shown superior properties, such as high strength and stiffness, combined with high aspect ratio suggest that they would make an effective strong superhydrophobic surface. Closely spaced nanowires protuberances introduce air troughs between individual nanowires, thus minimizing the effective area of contact between the water droplet and the nanowires film. The crystallographic structure of the nanowires flowers, was carried out by X-ray diffraction (XRD) and transmission electron microscopy (TEM) [2]. Both results indicate the crystallinity nature of the material with diffraction peaks and pattern consistent with β -SiC. The CA θ_r on SiC nanowires film is 170 degree. The Wenzel equation $\cos \theta_r = r f_1 \cos \theta - f_2$ shows the relationship between the CA of a liquid on a smooth surface θ and on a rough surface θ_r , where r is the roughness factor and f_1 and f_2 are the fractions of the nanowires and air on the film respectively. High speed photography was used to capture the repeated contact and rebounding of the water droplet bouncing on the nanowires film, thus demonstrating its elasticity and flexibility nature. Restitution coefficient, ratio of velocities after and before bouncing shows an average of > 0.9. Because of the notable properties, we envision that the nanowires can be of potential use as coating of self-cleaning water proof surface, as lubricant in industrial processes and as cell motility in biological processes. REFERENCES [1] Z. W. Pan, Z. R. Dai, C. Ma, and Z. L. Wang., J. Am. Chem. Soc. 2002, 124, 1817. [2] Z.J. Li, H. J. Li, X. L. Chen, A. L. Meng, K. Z. Li, Y. P. Xu, L. Dai Applied Physics A, 2003, Vol. 76, pp. 637-640.

U8.15

Geometric Effect on the MILC Growth Rate. Young-Su Kim¹ and Seung-Ki Joo¹; ¹School of Material Science and Engineering, Seoul National University, Seoul, South Korea; ²School of Material Science and Engineering, Seoul National University, Seoul, South Korea.

High quality polycrystalline silicon is very critical part of the high quality thin film transistor(TFT) for display devices. MILC(metal induced lateral crystallization) is one of the most successful technologies to crystallize the amorphous silicon at low temperature(below 550°C) which can use conventional and large glass substrate. In this study, we observed that the MILC behavior changed when the amorphous silicon active pattern width was changed abruptly and explain that phenomena with noble MILC mechanism model. The 10nm thick Ni layers was deposited on glass substrate that has various amorphous silicon patterns on it. Then we annealed the sample at 550°C with RTA(rapid thermal annealing) machine and measured the crystallized length with optical microscope. The MILC rate was reduced dramatically and stopped for several hours(incubation time). And the incubation time increased as the amorphous silicon pattern width difference get larger. We can explain these phenomena with the tensile stress that was caused by volume shrinkage due to the phase transform from amorphous silicon to crystalline silicon.

U8.16

Coupled Grain-Boundary Diffusion Creep and Grain Growth in Thin Films by Mesoscale Simulation.* Rong Ding¹, Dorel Moldovan², Vesselin Yamakov³, Dieter Wolf¹ and Simon Phillpot⁴; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Department of Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana; ³National Institute of Aerospace, Hampton, Virginia; ⁴Department of Materials Science and Engineering, University of Florida, Gainesville, Florida.

Mesoscale simulations of grain-boundary (GB) diffusion creep (Coble creep) accommodated by GB migration in columnar thin films were performed using the finite element method based on the variational principle of dissipated power. The effects of microstructural inhomogeneity, including topological (i.e., a grain-size distribution) and physical inhomogeneity (i.e., the distribution in grain-boundary mobility and diffusivity), were investigated. Assuming that the grain boundaries exhibit no sliding resistance in response to shear stress, the variation of the normal-stress distribution and the diffusive flux along the grain boundaries during Coble creep were analyzed. The simulations reveal that a topologically inhomogeneous microstructure remains stable even at high strains because of the accommodation by grain-boundary migration, to relax the stress concentration in the microstructure. During deformation grain growth occurs due to GB migration and grain switching. This coupling between the GB diffusion creep and grain growth keeps the grains nearly equiaxed at high strains. *Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-31-109-Eng-38.

U8.17

Growth, Crystal Structure and Stability of Ag-Ni/Cu Films. Igor Bdkin^{1,2}, G.K. Strukova², G.V. Strukov², V.V. Kedrov², D.V. Matveev², S.A. Zverkov² and A.L. Kholkin¹; ¹Department of Ceramic and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal; ²Institute of Solid State Physics, Chernogolovka, Moscow distr., Russian Federation.

Ag_x-Ni_{1-x} film alloys on Cu substrates with any compounds (x=0.0-1.0) are grown by electrodeposition in organic solvent. Only few reports about electrodeposition synthesis of nanocrystalline two-phase alloys with nickel: Ni-Co [1], Ni-W [2], Ni-Fe [3,4]. Mechanical alloying Ni and Ag fabricated nanostructure [5]. According to the equilibrium phase diagram, mutual solubilities of silver and nickel virtually zero [6] and therefore co-deposition of these elements is especially congenial for grown microcrystalline alloys. Crystallographic properties of the grown films were studied by X-ray diffraction and by transmission electron diffraction microscopy techniques. Variations of alloy structure are possible by change of salts concentration in the solution and voltage between electrodes. It was found, that at the contents Ni in an alloy more than 10% is observed the broadening of the X-ray diffraction peaks. We explain it by formation nanosize grains of the alloy (<10nm), that compounded with electron microscopy researches. The size of grains of the alloy depends on concentration (with 3.0-3.5nm for alloys near Ag_{0.3}-Ni_{0.7} compound). Stability of Ag-Ni alloys we have examine in temperature interval 20-600°C on air. The transformation of alloys was found at 100°C, accompanying with increase of grain sizes. Under heating the X-ray diffraction peaks are narrowed. This effect monotonically varies up to 600°C. The annealing under stable temperature did not change X-ray spectrums. The effect can be explain as recrystallization in this film and stability of alloy grains with temperature depend from grain size. Thus, the electrochemical method is very convenient for the fabrication these nanocrystalline alloys. [1] H. Zhu, S. Yang, G. Ni, D. Yu, and Y. Du, Scripta Materialia 44, 2291 (2001) [2] T. Yamasaki, Scripta Materialia 44, 1497 (2001) [3] F. Czerwinski, Electrochimica Acta 44, 667 (1998) [4] F. Czerwinski, H. Li, M. Megret, and J.A. Szpunar. Scripta Materisli 37, 1967 (1997) [5] Z.L. Zhao, Y. Zhao, Y. Niu, C.L. Wang, and W.T. Wu, Journal of Alloys and Compounds 307, 254 (2000) [6] M.Hansen, Constitution of Binary alloys (McGraw Hill, New York, 1958)

U8.18

The Residual Stress Effect on Microstructure and Optical Property of ZnO Films Produced by RF Sputtering. Youngman Kim and Sang Ryu; Materials Science and Engineering, Chonnam National University, Gwangju, South Korea.

ZnO films were produced on the Si(100) wafer by RF sputtering in terms of processing variables such as substrate temperature and RF power. The stress in the films was obtained from the Stoney's formula using a laser scanning device. The stress levels in the films showed the range from 20MPa to -700 MPa depending on processing variables. The specimens were thermally cycled from R.T. to 250 C to investigate the stress variation as a function of temperature. The stress in the film showed no general trend according to processing

parameters presumably due to the competing combination of stress generation and relaxation factors during thermal cycling. AFM and SEM were employed to characterize the microstructure of the films. As the substrate temperature increased, the film surface became rougher and the films showed coarser grains. The optical property of the films was studied by PL measurements. At the highest substrate temperature 800 C the film exhibited sharp UV peaks unlike other conditions.

US.19

Residual stress and microstructural evolution in thin film materials for a microfabricated solid oxide fuel cell (SOFC).

David Quinn^{1,2}, Mark Spearing² and Brian Wardle²; ¹Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Aeronautics and Astronautics Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Stability of multilayered membrane structures is a major challenge in the development of microfabricated solid oxide fuel cells. An important parameter required to guard against mechanical instability and failure in the structural design of micro SOFC membranes is the residual stress state in the deposited materials. The work presented here explores residual stress in sputter deposited yttria stabilized zirconia (YSZ) thin films (200nm - 1000nm thickness) as a function of deposition conditions, including deposition pressure, temperature and gas environment. Results indicate working pressure to be the predominant process parameter in controlling residual stress. Variations in working pressure result in residual stress levels ranging from several hundred MPa compressive to mildly tensile. The evolution of residual stress with working temperature is investigated by thermally cycling YSZ films deposited on silicon wafers. Observed changes in the intrinsic residual stress of the film serve as indicators of possible changes in microstructure. Such microstructural changes are subsequently characterized using x-ray diffraction at room and elevated temperatures as well as atomic force microscopy of as-deposited and annealed films. Correlations with relevant mechanisms and models of residual stress evolution are discussed. Finally, it is outlined how this and similar data is used in fabrication process control and in the structural analysis and design of multilayered membranes to ensure mechanical stability of micro SOFC devices.

US.20

Structure and Stability of Nano-multi-layer of Metals and Oxides.

Somei Ohnuki¹, Tomohiko Ohkoshi¹, Yuko Kakuta¹, Takanori Suda¹, Seiichi Watanabe¹ and Masahiko Ishino²; ¹Materials Engineering, Hokkaido University, Sapporo, Japan; ²Kansai-Res., Japan Atomic Energy Research Institute, Kizu, Kyoto, Japan.

High-resolution microscopy and X-ray refraction were applied for surveying thermal and environmental stability in nano-multi-layer materials, which are candidate for soft X-ray mirror materials. < c-Mo/a-Si multi-layers > (1) Transition layer: The multi-layer structure was stable under thermal annealing up to 400 C. Amorphous structure with 1-2 nm thickness appears at the interface, which has a dark contrast comparing with a-Si layers. The inter-mixing at low temperature may produce the transient layer. (2) Irradiation-induced amorphization: We tried to accelerate local diffusion using electron-irradiation in HVEM at room temperature. During in-situ observation the transition layer grew from the interface finally the whole of multi-layer became amorphous structure. (3) Diffusion-assisted void formation: Tiny voids (<1 nm) developed at the interface and then line up at the center of the a-Si layer. This is a result of Kirkendall effect, which means that an intensive diffusion of Si toward c-Mo occur, even at room temperature. < Co3O4 Oxide nano-layers > (4) Co3O4 / SiO2 nano-layer: This system shows good X-ray refraction property, and has a flat structure at nano-scale, where the thermal stability was high up to 600 C. (5) Co3O4 / BN nano-layer: This showed bad X-ray refraction property, and has a nano-particle structure of Co3O4. Such difference may be caused by less wettability and chemical affinity. (6) Thermal stability at high temperature up to 700 - 1000 C: The nano-particle structure in Co3O4 / BN system up to 600 C, where such high stability consists with qualitative thermodynamic data, even if nano-scale particles.

US.21

Mechanical Stability of Thin Self-Supported Nanocrystalline Ceramic Films. Igor Lubomirsky, Materials & Interfaces, Weizmann Institute of Science, Rehovot, Israel.

Nanocrystalline self-supported films of functional ceramic materials, for instance, ferroelectrics or ionic conductors, are very promising components for a large variety of microelectronic and micro-electro-mechanical devices. We have investigated mechanical stability of nanocrystalline self-supported structures of CeO₂ and BaTiO₃ that were 200-800 nm thick and had lateral dimensions of 100-500 μm. It was found that mechanical stability of nanocrystalline

self-supported films depends on a number of factors, among which spontaneous intergrain strain, chemically induced stress and rearrangement of elastic domains are the most influential. In self-supported films of CeO₂ all three factors are important, because pure or doped CeO₂ may undergo a series of successive phase transitions and/or spontaneous continuous changes of the lattice parameter. Incoherent expansion and contraction of the neighboring grains leads to accumulation of an intergrain stress reaching up to a few GPa. Accumulating stress, affects oxygen equilibrium in the material and order/disorder transition of oxygen vacancies. As a result a dynamic crystallographic texture may be formed. These effects may lead to abrupt changes in shape and macroscopic stress in freestanding films. In nanocrystalline, self-supported films of BaTiO₃, intergrain strain and stress-induced reorientation of ferroelectric grains are strong enough to cause rapid (10-20 sec) changes. Interestingly, if the film does not disintegrate, one can observe the changes repeatedly. The influence of the above mentioned effects is not unequivocal and depends on the preparation route. Therefore, accumulation of knowledge about the chemical and mechanical properties of self-supported nanocrystalline structures promises their successful practical application in the near future.

US.22

Nano-Structured Ultra-Hard Al-Si Films Synthesized by High Rate Codeposition.

Velimir Radmilovic¹, David Mitlin² and Ulrich Dahmen¹; ¹LBNL-NCEM, MS-72, University of California, Berkeley, California; ²Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada.

We used high rate electron-beam co-evaporation to synthesize single phase and dual phase Al-Si thin films displaying remarkable mechanical properties and microstructural stability. The composition of these films was varied from 2 to 23at.%Si. These films were compared with pure Al films grown using identical deposition conditions that were used as a baseline. With increasing Si content the nano-indentation hardness increased from 1 GPa for the pure Al film to 4 GPa for the film containing 23at.%Si. Analysis of the indents indicated that all samples exhibited plasticity during deformation. We analyzed the films' microstructure using conventional, atomic resolution and analytical transmission electron microscopy. The microstructure of the alloy films was an order of magnitude finer than that of pure Al, with grain sizes in the range from tens to several hundreds of nanometers. We demonstrate that the nano-scale Si phase is effective in pinning the microstructure during elevated temperature aging. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

SESSION U9: Time Dependent Failure Processes

Chairs: Taher Saif and Richard Vinci

Thursday Morning, December 2, 2004

Room 210 (Hynes)

8:30 AM U9.1

Mechanical Properties of Electrophoretically-Deposited CdSe Nanocrystal Films.

Shengguo Jia, Mohammad Islam, Yuqi Xia, Robert J. Broesler Jr., Ben Smith, Richard Robinson, Joze Bevk, Jeffrey Kysar and Irving P. Herman; MRSEC, Columbia University, New York, New York.

Approaches to measuring and then minimizing the strain in electrophoretically deposited CdSe nanocrystal films are investigated. Under some conditions, cracking and delamination are seen for films thicker than a critical thickness (~0.8 microns for 3.2 nm nanocrystals), as seen by SEM and AFM, and this is attributed to high strain energy in this film. Fourier Transform Infrared Spectroscopy (FTIR) and Raman scattering are used to measure film strain in strained and strain-relieved films. The deposition conditions are varied to minimize this strain, which is thought to be due to the evaporation of residual hexane solvent after electrophoretic deposition, which changes the equilibrium separation of the nanocrystal cores. These CdSe nanocrystal films are seen to become mechanically stronger and more resistant to chemical dissolution after being treated by cross-linker molecules such as 1,6-hexanedithiol and 1,7-heptanediamine. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award No. DMR-0213574 and by the New York State Office of Science, Technology and Academic Research (NYSTAR).

8:45 AM U9.2

Failure of Brittle Functional Layers on Flexible Devices.

Piet Bouten¹, Judith de Goede¹, Yves Leterrier², Leonard Medico² and Jan-Anders Manson²; ¹Philips Research Laboratories, Eindhoven, Netherlands; ²Laboratoire de Technologie des Composites et

In recent years an increasing amount of attention is given to the development of flexible electronic devices, such as flexible displays and microelectronics on flexible carriers. Instead of the brittle carriers (glass and silicon) more flexible substrates, such as polymers and thin metal sheet are used. The functional performance of the device requires, however, still thin brittle layers. Examples of these layers are a transparent conductor like Indium Tin Oxide (ITO) in flexible displays, transparent inorganic hermetic coatings in OLED devices and silicon-based microelectronics in flexible, active matrix driven, Liquid Crystal Displays (LCD). Mechanical failure of the brittle functional layers seriously limits the allowed deformation of the flexible devices. In the present study, conducting ITO layers are used to study the failure behaviour of the tensile loaded thin brittle layer. In a two-point bending test the resistance of uniform 100 nm ITO layers and narrow ITO lines (10-300 μm width) is determined as a function of the applied tensile strain. At a certain applied strain the resistance increases strongly. This characteristic strain is analysed on a large number of samples. Statistical data show two effects: a small effect of the ITO line-width on the measured characteristic strain and a significant change in the width of the strength distribution. For a uniform layer and wide ITO lines a narrow strength distribution is obtained, for narrow ITO lines a significantly wider strength distribution is reported. The experimental results are discussed in relation to the failure mechanism of thin brittle layers. Stable cracks of a limited length are initiated at defects in uniform brittle layers. At a critical strain ϵ_p the crack length is no longer stable; it propagates over the whole width. The length of the stable crack depends on the layer thickness h , the actual strain level ($\epsilon < \epsilon_p$) and the elastic mismatch between substrate and layer. For a high modulus layer on a polymer substrate this stable length is significantly larger than the layer thickness. For the presently tested 100 nm layers stable cracks may be 10-100 μm range are observed. The wide failure strain distribution of the narrow lines is determined by the distribution of weak spots. The narrow failure strain distribution of the wide ITO lines is determined by the well-defined crack propagation strain ϵ_p . Different mechanisms are responsible for the electrical failure of wide and narrow ITO lines on mechanical loaded flexible display substrates. These mechanisms are also active in other types of brittle functional layers, such as hermetic inorganic coatings and silicon-based microelectronics. The consequences are, however, quite different. The effect of a single stable crack in a uniform ITO layer has an insignificant effect on the conductivity of the layer. A single defect in a hermetic layer, however, reduces the barrier properties of the layer directly.

9:00 AM *U9.3

Accelerated Cracking in Complex Device Structures.

Reinhold Dauskardt, Stanford University, Stanford, California.

Debonding of interfaces and cracking of fragile interlayer dielectrics effects the mechanical integrity of a wide range of thin-film device structures. This results in reduced yield at all levels of device processing including survival through chemical mechanical planarization (CMP) and subsequent device packaging. Two unique challenges for the next technology nodes involve the introduction of new ultra low k dielectric materials and the effect of interconnect architecture including length-scales and aspect ratios, on mechanical and fracture behavior. Materials are nearly always optimized for other desired properties (e.g. dielectric properties or diffusion resistance) and the resulting effects on mechanical performance can be significant. In this presentation, the mechanical and fracture behavior of representative blanket and patterned thin-film interconnect structures including glass and organic dielectrics, barriers and metal layers, are examined. Survival through processing that exposes these structures to complex chemical environments is explored in terms of the kinetics of accelerated environmentally-assisted cracking. The significant effect of aqueous CMP slurry chemistry on the rate of cracking of ultra low k porous dielectric glasses is considered. The surprising acceleration of crack growth rates in post CMP cleaning solutions is presented. Ideas for interfaces that inhibit such debonding are suggested. The effects of interface parameters and thin-film composition and porosity will also be considered. Models to explain the effect of interface morphology and chemistry, ductile metal or dielectric layer thickness, elastic properties and thickness of the barrier layer, and loading mode are reviewed. Novel strategies to toughen fragile nanoporous materials using molecular remnants of the porogen molecules used to create the porosity are described. Finally, the effect of more complex patterned thin-film structures are examined where length scales are restricted in more than one dimension. Implications for device reliability, integration of new materials, and life prediction are discussed.

9:30 AM U9.4

Cracking in Interconnects due to Thermal Ratcheting by Extended Finite Element Method. Zhen Zhang¹, Jean H.

Prevost² and Zhigang Suo¹; ¹DEAS, Harvard University, Cambridge, Massachusetts; ²Civil & Environmental, Princeton University, Princeton, New Jersey.

Cracks usually nucleate and propagate in microelectronic devices after hundreds or thousands of thermal cyclic loading. The origin of high stresses and crack behavior in the brittle thin film, which is usually packaged by compliant polymer, was a mystery. The present paper analyzes a three-layer structure consisting of an elastic film, an elastic-perfectly-plastic metal underlayer stripe, and a semi-infinite bulky elastic substrate. The thermal mismatch between the metal layer and the substrate causes metal stripe yield in every thermal cycle. Under certain circumstances, the plasticity ratchets in the same direction as the temperature cycles. The stresses in the top brittle layer are built up by this ratcheting deformation, hence cracks advance if its fracture toughness is reached. This mechanism was first found by Huang et. al. (JMR 15:1239(2000)). But the simulation of stress build-up and crack propagation in the brittle film was never done since the nonlinearity of plasticity and the crack growth are two arduous tasks. In this paper, XFEM (extended finite element method), first invented by Moës et al (IJNME, 46:131(1999)), is used to simulate these processes in the thin film and the evolution of ratcheting in the metal layer simultaneously without remeshing, based on the shear lag model for multilayer structure. The metal layer ratchets like viscous flow. So the stress field in the film relaxes in the crack wake and intensifies around the crack tip. The stress intensity factor is proportional to the square root of a length scale, which is introduced by linear creep analogy with ratcheting under certain conditions. The scaling law for the steady-state crack velocity is also identified. The crack growth in interconnects (SiN film over Al pad) is investigated and shows the same result as that from experiments. Initially, the cracks are put in the thin film in random positions with random orientations and random length. Then the cracks start to grow if the stress intensity factor is equal to fracture toughness, and remain stationary if under compression. The growth paths follow mode I in the film over aluminum pad, and propagate along the boundary if the crack tip encounter the boundary line of metal stripe and substrate since the stress in the SiN film over Si substrate is too low to propagate the crack. All of this is coincident with experiments. Finally, the pros and cons of the linear creep analogy are discussed.

9:45 AM U9.5

Sub-Critical Telephone Cord Delamination Propagation.

Alex A. Volinsky¹, Patrick Waters¹, James D. Kiely² and Earl Johns²; ¹Mechanical Engineering, University of South Florida, Tampa, Florida; ²Seagate Technology, Pittsburgh, Pennsylvania.

Argon pressure significantly affects the residual stress in sputter deposited thin films and coatings. In case of W thin films, high residual stresses on the order of 1 GPa are quite common. With the rest of sputtering parameters being equal, argon pressure determines the sign and the value of residual stress. When the amount of stored elastic energy in the film due to the residual stress exceeds the interfacial toughness, fracture normally occurs. Telephone cord morphology is commonly observed in delaminating thin films under residual compressive stresses. Here, biaxial film stress is partially relieved by film buckling in the direction perpendicular to the telephone cord propagation, and by "secondary" blister buckling in the direction of telephone cord propagation, which results in the sinusoidal fracture patterns. Normally telephone cord blisters "run out of steam" and stop once the interfacial toughness exceeds the strain energy release rate. It is possible to make blisters propagate further by either putting mechanical energy into the system, or by introducing liquids at the crack tip, thus reducing the film interfacial toughness. Stress-corrosion cracking causes W thin film delamination, and is readily observed in vintage mirrors. Crack propagation rates on the order of microns per minute were measured for W thin films in different fluid environments. Telephone cord buckling delamination presents a test vehicle for studying crack propagation rates and stress-corrosion cracking in thin films.

10:30 AM U9.6

Activation Pathways of Crack Tip Instability and Chemical Effect. Ting Zhu¹, Ju Li², Sidney Yip³ and Zhigang Suo¹; ¹Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; ²Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio; ³Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Using molecular orbital theory and empirical potentials, we analyze thermally activated processes of crack-tip dislocation loop emission in Cu, cleavage bond ruptures in Si, and stress corrosion in SiO₂ by water. In all cases nudged elastic band and/or dimer methods of sampling reaction pathways, guided by intuition from deformation mechanics in solids, are adopted to determine the minimum energy paths, saddle point energies and corresponding atomic configurations.

In Cu at 75% of the athermal critical strain energy release rate for spontaneous dislocation nucleation, we find a higher activation energy than the continuum level estimate which we attribute to ledge production effects on the crack front. In Si we obtain kink formation and migration energies for different crack front orientations on the (111) cleavage plane to rationalize an observed characteristic anisotropic crack propagation. In a strained silica nanorod (mimicking an actual crack front environment) we map out activation pathways for hydrolyzing the Si-O-Si bridge, revealing three competing mechanisms of hydrolysis reaction, as well as giving stress-dependent activation energies that are rate-controlling. Implications concerning chemically assisted kinetic crack growth will be discussed.

10:45 AM U9.7

Mode-I and Mixed-Mode Fracture of Tetrahedral Amorphous Diamond Like Carbon (ta-C) MEMS.

Krishna N. Jonnalagadda¹, Ioannis Chasiotis¹, Thomas A.

Friedmann² and John P. Sullivan²; ¹Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia; ²Sandia National Laboratories, Albuquerque, New Mexico.

The Mode-I fracture toughness of tetrahedral amorphous diamond-like carbon (ta-C) MEMS has been obtained for the first time via direct measurements of displacement fields in the vicinity of atomically-sharp cracks and by using linear elastic fracture mechanics (LEFM) solutions. Furthermore, mixed-mode (Mode-I and Mode-II) fracture toughness studies on MEMS-scale specimens were conducted with a new approach that allowed generating small kinks at the end of edge cracks. Mode-I fracture toughness measurements were performed with atomically sharp edge cracks in finite width uniform tension MEMS-scale specimens. The mathematically sharp cracks that varied in length between 20-30 microns were generated by indenting a SiO₂ sacrificial layer using a micro-hardness tester. Typical specimen gage sections were 100 microns wide and 1 micron thick and were loaded in tension *in situ* under an AFM. The crack tip displacements, obtained in the vicinity of atomically sharp cracks using the Atomic Force Microscopy/Digital Image Correlation (AFM/DIC) method, were compared to the edge crack displacement fields predicted by linear elastic fracture mechanics (LEFM) at different crack tip stress intensities. The measured Mode-I fracture toughness of ta-C, averaging 4.1 ± 0.3 MPa \sqrt{m} , was found to be independent of crack length. This fracture toughness value is four times that of polysilicon and is comparable to those of single crystal diamond (111) 4.0 MPa \sqrt{m} , microcrystalline diamond 4.9 MPa \sqrt{m} , and ultrananocrystalline diamond 4.6 MPa \sqrt{m} . Furthermore, the Mode-II fracture toughness of ta-C was calculated using edge pre-cracks with a small kink at the crack tip in conjunction with mixed-mode elastic fracture analysis. A 200 nm polysilicon buffer layer deposited between SiO₂ and ta-C was instrumental in the formation of small kinks at the end of edge cracks. Sufficiently far from the indentation point, the stress mismatch between ta-C and polysilicon was the dominant driving force that caused the propagating pre-crack to abruptly change its direction and finally be arrested. Then, the normal and tangential stresses on the crack surface as well as the local stress intensity factors at the crack tip were computed and used in the calculation of the Mode-II fracture toughness for ta-C.

11:00 AM U9.8

Composition Effects on Mechanical Properties and Fracture Behavior of Low-k Organosilicate Glass (OSG) Thin Films.

Youbou Lin, Yong Xiang and Joost Vlassak; DEAS, Harvard University, Cambridge, Massachusetts.

Non-traditional Inter-Layer Dielectric (ILD) materials with low dielectric constants (low-k) are needed for deep submicron integrated circuit fabrication. Organosilicate glass (OSG) is currently the leading candidate among new low-k dielectric materials. OSG is obtained through incorporation of organic groups such as terminal methyl groups into a silica glass network. The organic groups reduce the dielectric constant, but also degrade the mechanical properties of the material. The low fracture toughness, in particular, makes the material difficult to integrate and may result in channel cracking and delamination during processing. The carbon content and network structure of the OSG play a critical role in determining the mechanical behavior of the material. In this study, OSG thin films of different carbon content are prepared using Chemical Vapor Deposition (CVD). Structural and compositional information is obtained using Rutherford Backscattering Spectroscopy (RBS), Wavelength Dispersive Spectroscopy (WDS), and Fourier Transform Infrared Spectroscopy (FTIR). The mechanical properties and fracture behavior are measured as a function of carbon content using the bulge test and four-point bending technique. The effect of carbon content on the structure and hence the mechanical properties of the films will be discussed.

11:15 AM U9.9

High-Cycle Fatigue in Freestanding Thin Film Metal Test

Structures. Maarten P. de Boer¹, Alex D. Corwin¹, Ghatu Subhash^{1,2} and Michael J. Shaw¹; ¹Reliability Physics, Sandia National Labs, Albuquerque, New Mexico; ²Mechanical Engineering, Michigan Technological University, Houghton, Michigan.

The elastic, plastic and interfacial properties of freestanding metal thin films are of interest in MEMS applications such as radio-frequency devices, microrelays and optical reflectors. In this work, we have developed a new methodology to measure strength, hysteresis, fatigue and creep properties of metal thin films. The test structure we have used is a freestanding fixed-fixed Al/0.5% Cu beam of 0.7 micron thickness with a stress concentrating notch. We focus here on high-cycle fatigue, which is crucial in MEMS applications where fatigue often cannot be tolerated. The structure was actuated electrostatically and was monitored stroboscopically with phase-stepping interferometry, allowing in-situ full-field nanometer-scale deflection information to be obtained. The resonant frequency of the structure was 70 kHz. Fatigue testing was performed at 10 kHz, allowing 10 million cycles to be accumulated in 20 minutes. We first actuated and modeled adjacent, simple fixed-fixed beams to find a value of 57 MPa residual tensile stress. The nominal stress concentration factor in the notched device was 5.33, giving a 304 MPa applied stress assuming Young's Modulus is 70 GPa (the applied stress values we report are engineering stress values - they overestimate the true stresses because plasticity, which leads to stress relaxation, is not taken into account). Some of the notched devices exhibited cracks due to the residual tension while others did not. These latter structures, which evidently have experienced some plastic stretching, were now further examined. A single-cycle test was first performed to find hysteresis, as defined by a difference in the loading versus unloading deflections during a single actuation cycle in which an additional stress was applied. The hysteresis threshold was found at an additional applied stress of 66 MPa. We then performed fatigue tests and observed a log-linear trend in deflection amplitude versus fatigue cycles at an additional applied stress from as low as 51 MPa. These fatigued films displayed no obvious damage by SEM, indicating that the fatigue is in the subthreshold regime. More detailed SEM analysis and the results of creep experiments will be reported. Acknowledgment: 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.

11:30 AM U9.10

Ultra high-cycle fatigue in pure Al thin films. Christoph Eberl¹,

Ralph Spolenak¹, Oliver Kraft², Franz Kubat³, Werner Ruile⁴ and Eduard Arzt^{1,5}; ¹Max-Planck-Institut fuer Metallkunde, Stuttgart, Germany; ²Forschungszentrum Karlsruhe, Karlsruhe, Germany; ³Technische Universitaet Clausthal, Clausthal, Germany; ⁴EPCOS AG, Muenchen, Germany; ⁵Institut fuer Metallkunde der Universitaet Stuttgart, Germany.

The trend of shrinking structural size, rising frequency and driving power in mechanical devices leads to a steady increase of energy density. In Surface Acoustic Wave test devices, pure Al thin films are stressed mechanically at frequencies in the GHz regime, which induces a characteristic void and extrusion formation. By the use of acoustic resonators, patterned Al thin films (400 nm) were fatigued at 900 MHz. Analytical models enabled us to relate the electrical power to the induced cyclic stress amplitude. The life time of Al thin films for up to 10^{14} cycles could be measured. *In situ* observations (SEM) of extrusion and void formation combined with microstructural post-test analysis (FIB) indicate a fast material transport at the grain boundaries. Measurements of the activation energy indicate that grain boundary diffusion plays a major role for material transport. The quantitative measurement of the defect formation showed a direct correlation between the resonance frequency of test devices and the extrusion density. The development of defect density versus time can be described by a simple model, which is a first step to the development of a physical life time model for the ultra high-cycle fatigue in metal thin films.

11:45 AM U9.11

Influence of Macro- and Nanotopography and Process Parameters on the Stability of Thermocompression Bonding.

Konstantinos Stamoulis¹ and S. Mark Spearing^{2,1}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²School of Engineering Sciences, University of Southampton, Southampton, United Kingdom.

Thermocompression bonding is a low temperature, thin film, wafer-level joining technique with great potential for packaging and the creation of 3-D interconnects. The process is a form of solid-state joining and requires the simultaneous application of temperature and pressure to wafers patterned with metallic thin films in order to bring the mating surfaces into atomic proximity. The quality of the resulting bond is critically dependent on the interaction between flatness

deviations that range from wafer bow to surface roughness, the thin film properties and the process parameters used to achieve the bonds. Hitherto there has been limited modeling applied to understand the relative contributions of these effects. This article presents a continuum model that examines the effect of flatness deviations at the wafer scale (macrotopography) and at the level of surface roughness (nanotopography). An analytical expression for the strain energy release rate associated with the elastic deformation required to deform the wafers into a common curvature in order to overcome the effect of wafer bow is developed. The modeling framework involves plate theory and interface fracture mechanics. Furthermore, a slip-line field solution is applied to analyze the pressure and temperature conditions required to flatten nano-scale asperities through local plastic deformation in order to achieve bonding over the full apparent area and to make high toughness bonds. The approach adopted is based on classical studies of contact yielding for rigid-perfectly plastic materials. The analytical results are compared to previous experimental data for gold thermocompression bonds. Key conclusions from the modeling and experiments include: (1) time-independent plasticity is the dominant deformation mechanism for current process conditions of gold and copper thermocompression bonding, (2) wafer bow has negligible effect on determining the variability of bond quality, (3) a local pressure of approximately three times the temperature-dependent yield stress must be applied in order to achieve a good bond in terms of interfacial contact and toughness. Recommendations are made for process control and patterning.

SESSION U10: Time Dependent Mechanical Behavior and MEMS

Chairs: Alex Volinsky and Maarten de Boer
Thursday Afternoon, December 2, 2004
Room 210 (Hynes)

1:30 PM *U10.1

Anelasticity and Creep in Nano Grained Aluminum and Gold Films. Taher Saif¹ and Jong Hee Han²; ¹Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We present a novel experimental method to study anelastic and creep response of nano grained thin (100nm) free standing metal films. The method consists of depositing metal films of desired thickness on silicon substrate, and cofabricating a free standing sample and a micro stage that can apply uniaxial tension on the sample. Co-fabrication of the sample and the micro sensor ensures uniaxiality of loading and avoids any assembly. The stage has in-built force and displacement sensor to measure sample stress and strain. The sample is strained by applying time dependent deformation on the stage by a piezo actuator. Temperature of the sample above the room temperature is controlled by a hot plate close to the micro stage, and measuring the temperature of the stage by a thermocouple. We apply the apparatus to measure stress-strain response of aluminum and gold films from room temperature to about 110C. We find that as grain size decreases below 50nm, elastic modulus of the metal films decreases, although the decrease in aluminum is small compared to that of gold. Transmission electron microscopy of the films shows small voids in the gold film, but no such void could be detected in aluminum. Stress-strain measurements at increasing temperatures indicate that the small reduction of elasticity in aluminum at room temperature cannot be explained by anelasticity. However, aluminum shows anelastic response in the temperature range of 75-110C. Its relaxed modulus is close to 66% of the unrelaxed modulus, and the activation energy is found to be 1.2eV when the grain size is 65nm. For the case of gold, lower elastic modulus at room temperature may be attributed to the voids in the film. Stress-strain experiments at various temperatures show strong creep response, i.e., the strain is permanent. The creep rate increases with temperature, as expected. Atomic force microscopy studies of both aluminum and gold films before and after tensile tests show little grain growth in aluminum, whereas, significant grain growth is observed in gold film, which may explain its large creep response.

2:00 PM U10.2

Stress Relaxation and Stress Non-Uniformity in Thin Gold Films between 25 and 100 oC. Walter L. Brown, Seungmin Hyun and Richard P. Vinci; MS&E, Lehigh University, Bethlehem, Pennsylvania.

We have studied stress relaxation in 100 and 200 nm thick Au films during temperature cycles and isothermally in the low temperature regime between 25 and 100 C. The films are e-beam deposited at room temperature with a 10 nm Ti adhesion layer onto tensile 210 nm thick SiN membranes 2x12 mm² or 3x12 mm² that form windows supported by a thick silicon surrounding frame. The stress in the

composite Au/Ti/SiN film is directly determined from the frequency of the lowest resonant mode of the membrane. The resonant frequency is typically between 10 and 40 kHz and can be determined to about 1 Hz in an electrostatically driven self-resonant electronic circuit. The Q of the resonance (the ratio of the resonant frequency to the frequency width of the resonance) is typically several thousand. The resonance provides very high sensitivity to stress changes. The stress in as-deposited Au films is slightly compressive. The compressive stress of the Au increases in the familiar way as the temperature is raised because of thermal expansion differences with the Si window frame. Relaxation of this compressive stress as well as of the less compressive stress that results after cooling from a hold at an elevated temperature (for example, 100 oC) has been measured. The relaxation rate and extent depend on film thickness and on details of the thermal history in ways that will be presented and discussed. In general, there is more relaxation than was seen for similar thickness Al films in this low temperature regime.1) An unexpected feature of the study has been the observation of sudden dramatic changes in the frequency width of the resonance during heating or cooling ramps. We had been looking for evidence of mechanical energy loss mechanisms as they might be revealed through changes of the Q of the resonance (as in an internal friction measurement) but the changes we observe are much too large and they do not always occur at the same temperature on repeated thermal cycles. We have concluded that they are due to the development of non-uniformities in stress over the area of the vibrating membrane (one region having a stress that would dictate a particular frequency and another area a different one). The resonance is therefore broadened inhomogeneously. Nonuniform stresses have been directly measured (at a fixed temperature) using x-ray microbeams.2) We suggest that the inhomogeneous stresses revealed in resonance arise from microstructural details (as in the microbeam studies) that result in build up and release of stress at particular sites as the average stress is being changed thermoelastically. 1) Seungmin Hyun et al App.Phys.Lett. 83, 4411 (2003) 2) R.Spolenak et al Phys.Rev.Lett. 90 096102 (2003)

2:15 PM U10.3

Anelastic Behavior of Thin FCC Metal Films. Seungmin Hyun¹, Tejpal Hooghan¹, Walter L. Brown¹ and Richard P. Vinci¹; ¹MS&E, Lehigh University, Bethlehem, Pennsylvania; ²Texas Instruments Incorporated, Dallas, Texas.

The strain rate dependent elastic modulus, and stress relaxation and recovery behavior of thin FCC metal films in the elastic regime at room temperature have been measured using a novel bulge system. Al, Cu and Au films of 1um and 100nm thickness were prepared by e-beam evaporation or by sputtering onto a silicon nitride membrane substrate. The membranes were either 2x12 mm² or 3x12 mm² supported by a thick frame of silicon. The films were strained with differential gas pressure and the bulge height as a function of pressure or time was determined from measurements of changes in capacitance between the film and a fixed electrode. At a strain rate of 10-4 /sec the modulus of the Al films is similar to the modulus of bulk Al. The modulus decreases at lower strain rates, indicating anelastic behavior with stress relaxation occurring during the strain loading and unloading portions of a pressure cycle. Pressure cycles with long holds at fixed pressure provide direct observations of stress relaxation (when the hold is at a high pressure) or stress recovery (when the hold is at a low pressure following an excursion to higher pressure). The relaxation and recovery behavior are highly dependent on the strain history of the films unless a long period (the order of a day) at zero pressure is provided for complete recovery. This anelastic behavior of Al thin films depends on film thickness and grain size. The relationship between the strain rate dependence of the modulus and the stress relaxation and recovery during long holds will be discussed. Results will also be presented for Cu and Au films.

2:30 PM U10.4

Determining Elastic Properties during in situ Deformation in the Swiss Light Source. Antonio Cervellino¹, Peter M. Derlet¹, Dan Gianola², Helena Van Swygenhoven¹ and Kevin J. Hemker²; ¹ASQ/NUM, Paul Scherrer Institute, PSI-Villigen, Switzerland; ²Dep. of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland.

In situ elastic deformation measurements of thin metallic films are performed in the materials beam line of the Swiss Light Source. The positions of several Bragg diffraction peaks are followed as a function of applied tensile load. Using this data and exploiting the unique geometry of the SLS powder diffraction apparatus, a theoretical analysis is presented that allows the determination of the elastic properties of the materials under investigation. The analysis procedure includes a weighted interpolation between the Voigt and Reuss assumptions on local strain and local stress continuity. Data for nanocrystalline Ni synthesized by electrodeposition and high-pressure-torsion, free standing Al films with thicknesses below 3 microns, and free standing thin polycrystalline Si are presented.

2:45 PM U10.5

Using *InSitu* Stress Measurement to Understand the Factors Controlling Relaxation, Dislocation Velocity, and Dislocation Density During III-V Heteroepitaxy. Candace Lynch¹, Eric

Chason¹, Rod Beresford¹ and Klaus Schwarz²; ¹Division of Engineering, Brown University, Providence, Rhode Island; ²IBM Research, Yorktown Heights, New York.

In situ stress measurements have been taken during MBE growth of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ and $\text{In}_x\text{Al}_{1-x}\text{As}/\text{GaAs}$ over a range of conditions in order to gain insight into the relaxation behavior of thin films grown on mismatched substrates. In the materials studied, stress relaxation occurs due to the formation and glide of dislocations. We find that relaxation never proceeds as far as predicted by models for relaxation which consider either the formation of isolated dislocations or periodic dislocation arrays, and explanations for this discrepancy between theory and experiment will be examined. Comparison to dislocation dynamics simulations which incorporate dislocation interactions yields good agreement, providing strong evidence that local phenomena can significantly affect the overall relaxation behavior, limiting the extent of plastic relaxation. The effect of temperature, growth rate, and growth interruptions on the relaxation rate has been explored, in the hope of developing a stronger understanding of the factors influencing both dislocation glide and the density of mobile threading dislocations. Relaxation during interruptions in the growth flux shows that relaxation is kinetically limited and that the relaxation rate is strongly affected by the adatom supersaturation during growth. During growth, the dislocation density does not initially increase to meet the demand for relaxation, and the density does not rise significantly until a thickness well beyond the equilibrium critical thickness, without a strong dependence on either temperature or growth rate. Once numerous dislocation sources are available, the dislocation density increases and balances the temperature-dependent glide velocity, yielding a total relaxation rate which is not strongly temperature-dependent.

3:30 PM U10.6

Crack Tip Displacement Field Measurements During Incremental Crack Growth in Polysilicon MEMS. S. W. Cho¹,

K. Jonnalagadda² and I. Chasiotis²; ¹Materials Science and Engineering, University of Virginia, Charlottesville, Virginia; ²Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia.

Local deformation fields at the tip of atomically sharp cracks in polycrystalline silicon MEMS have been recorded for the first time and compared with linear elastic fracture mechanics (LEFM) solutions. Based on these measurements, the effect of crystal anisotropy on incremental crack propagation in polycrystalline silicon MEMS was investigated. Dog-bone-shaped, polycrystalline silicon MEMS specimens with 2 microns thick and 50-400 microns wide gauge sections were fabricated using the MUMPs process. Atomically sharp edge cracks with lengths that varied between 6-23 microns were created in the micro-tension specimens using a micro-indenter. Direct measurements of Mode I crack tip displacement fields with nanometer resolution were conducted using *in situ* Atomic Force Microscopy (AFM)/Digital Image Correlation (DIC) method. The specimens used in the AFM/DIC measurements were 300 microns wide with edge cracks that averaged 14 microns in length. A series of crack tip displacement fields were acquired at different levels of stress intensity factor, K_I until it reached fracture toughness which was found to be equal to $1.03 \pm 0.07 \text{ MPa}\sqrt{\text{m}}$. The experimental crack tip displacement fields were found to be in excellent agreement with LEFM analytical solutions underscoring the accuracy of the measurements conducted in this work. Using the AFM/DIC method, direct experimental proof of incremental crack growth in brittle MEMS material was obtained for the first time via spatially resolved crack growth. Specifically, the incremental crack growth between individual polysilicon grains and the associated crack tip displacement fields were recorded at macroscopic stress intensity factor ($0.84 \text{ MPa}\sqrt{\text{m}}$), which was equivalent to the critical stress intensity factor for single crystal silicon cleavage planes. Small increments (1%) of stress intensity factor resulted in repeatable incremental crack propagation and crack arrest. Finally, the crack grew catastrophically at stress intensity factor, $K_{Ic} = 1.06 \text{ MPa}\sqrt{\text{m}}$, which was very close to the average fracture toughness recorded for polycrystalline silicon. Further validation for these observations was provided by the corresponding crack tip displacement fields acquired at each crack increment. The incremental crack growth in brittle polycrystalline silicon is attributed to its crystalline structure and the associated cleavage anisotropy. Crack propagation is controlled by grain boundaries and the varying orientations of adjacent grains that result in crack tip shielding and the enhanced macroscopic fracture toughness of polycrystalline silicon compared to that of single crystal silicon.

3:45 PM U10.7

Electrical Stability of Platinum Thin Films used in High Temperature MEMS Sensors. Mark P. McNeal, Martin U. Pralle, Anton C. Greenwald, Irina Puscasu, Ramesh Patel, James T. Daly and Edward A. Johnson; Ion Optics, Inc., Waltham, Massachusetts.

Stable thin film metal conductors are required for MEMS based micro-bolometric sensors and other devices operating at temperatures between 300 and 500°C. At these temperatures most thin film metallization for semiconductor circuits exhibit sustained drift in resistance. This change causes sensor output to drift, inaccurate readings, and reduced reliability. In this work we show that choice of adhesion metal and optimized annealing conditions reduce resistance drift by several orders of magnitude. Improved stability is attributed to the microstructural evolution during annealing, characterized by grain growth, and the coalescence and stabilization of a secondary phase. Cross-sectional TEM (transmission electron microscopy) and energy dispersive X-ray spectroscopy are used to analyze microstructure and compositional changes. Partially funded by the department of Energy, USA.

4:00 PM U10.8

Insensitivity of the Elastic Modulus to High Temperature Annealing in Tetrahedral Amorphous Carbon Films.

J. P. Sullivan, D. A. Czaplewski and T. A. Friedmann; Sandia National Labs, Albuquerque, New Mexico.

An interesting mechanical effect has been observed in tetrahedral amorphous diamond-like carbon (ta-C) films in which the density-normalized elastic modulus (E_Y/ρ) remains remarkably constant following annealing to temperatures approaching 1300 K. Tetrahedral amorphous carbon films are expected to behave similarly to other glassy networks in which the elastic moduli depend on the mean network coordination (the average number of neighbors connecting each atom or structural unit). For low temperature annealed pulsed-laser deposited ta-C films with about 80% 4-fold coordinated carbon, the measured Young's modulus is about 700 GPa, which agrees favorably with the modulus predicted by the amorphous carbon network model of Robertson. High temperature annealing can result in a number of structural changes in these films, ranging from minor structural relaxation for films that have high initial 4-fold concentration to near full conversion of the 4-fold carbon to 3-fold carbon (creating a material similar to graphitic glassy carbon) for films that start out with an initial 4-fold concentration less than 80%. If high temperature annealing converted the majority of the 4-fold carbon to 3-fold, theoretical predictions that take into account the expected decreases in both E_Y and ρ would suggest a softening in (E_Y/ρ) of nearly 80%. Experimental determination of (E_Y/ρ) in ta-C was made from measurements of the resonant frequency versus length of micro-electromechanical systems (MEMS) cantilever oscillators fabricated out of 1 μm thick ta-C films. Post-processing annealing of the MEMS cantilevers at temperatures up to 1300 K for 2 hours was performed, and the sp^3/sp^2 content was measured by transmission electron energy loss spectroscopy (EELS). Remarkably, the resonant frequencies of the oscillators were nearly unchanged, suggesting a near constancy of E_Y/ρ . These results indicate that either there are little or no structural changes occurring in ta-C annealed at temperatures as high as 1300 K, or, if structural changes are occurring, the elastic modulus remains unexpectedly high, i.e. over ten times greater than the E_Y observed for glassy carbon films, about 32 GPa. From a practical perspective, the experimental observations indicate that mechanical oscillators fabricated from ta-C are stable following very high temperature transients, suggesting their possible utility for applications at high temperatures. 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.

4:15 PM U10.9

OELIM methodology for determination of shape changes in MEMS structures. Ryszard J. Pryputniewicz¹, Thomas F.

Marinis², Joseph W. Soucy², Adam R. Klemperer¹, Peter Hefti¹ and Cosme Furlong¹; ¹Mechanical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts; ²Draper Laboratory, Cambridge, Massachusetts.

Development of MEMS inertial sensors and their packaging for high performance applications requires a balanced approach combining analyses with testing and measurements. There are too many unknown parameters, e.g., material properties, process conditions, and component/package interfaces, to rely solely on analyses during the development. Also, inherent characteristics of MEMS processes may lead to undesired shape changes, mechanical response, thermal behavior, and electrical performance. Recent advances in optoelectronic laser interferometric microscope (OELIM) methodology offer a considerable promise for effective determination of shape changes in MEMS structures; detailed knowledge of these changes

may facilitate optimization of packaging for advanced MEMS inertial sensors. Using OELIM methodology, sub-micron shape changes of MEMS structures are readily measured with nanometer accuracy and very high spatial resolution over a range of operating conditions. This greatly facilitates characterization of dynamic and thermomechanical behavior of MEMS components, MEMS packaging, and other complex material structures. In this paper, the OELIM methodology, which allows remote, noninvasive, full-field-of-view measurements of shape changes in near real time, will be presented and its viability for the development of MEMS structures will be discussed. These discussions will be illustrated by representative results that have been obtained while working to improve the packaging for MEMS inertial sensors.

4:30 PM U10.10

Strain Rate Dependence of the Elastic Modulus of Freestanding Aluminum and Gold Microbeams.

Paul A. El-Deiry, Nicholas Barbosa III, Ming-Tzer Lin, Richard R. Chromik, Walter Brown and Richard P. Vinci; Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania.

Al freestanding microbeams 600 μm long, 100 μm wide, and with thicknesses of 0.25 μm , 0.50 μm , 0.75 μm , and 1.00 μm , and Au microbeams 1.30 μm thick were tested under uniaxial tension at a variety of strain rates. Displacement controlled experiments employing five strain rates between $1 \times 10^{-3} \text{ s}^{-1}$ to $2 \times 10^{-1} \text{ s}^{-1}$ were performed on a custom-built microtensile system. A total crosshead displacement of 1.00 μm was exercised in order to remain in the elastic portion of the stress/strain curve. The Al microbeams of 0.50 μm and 1.00 μm thicknesses show an increase in effective modulus with increasing strain rate, but the 0.25 μm and 0.75 μm Al microbeams do not. The 0.25 μm film and the 0.75 μm film have similar grain sizes and similar moduli; the 0.50 μm and the 1.00 μm films have similar but smaller grain sizes and higher effective moduli. It appears that grain size plays a more dominant role than film thickness in determining the effective modulus behavior for Al. The 1.30 μm Au films do not exhibit a dependence of effective modulus on strain rate. The absolute value for the effective modulus of the Au microbeams is also higher than that for all of the Al films. These results will be discussed in terms of possible mechanisms controlling fast stress relaxation.

4:45 PM U10.11

Stress Hysteresis and Thermal-Mechanical Behavior of PECVD Silicon Nitride and Ebeam Aluminum Films for Microbolometer Applications. Shusen Huang and Xin Zhang; Manufacturing Engineering, Boston University, Boston, Massachusetts.

Recent advances in micro-electro-mechanical systems (MEMS) have led to the development of uncooled cantilever-based microbolometer arrays, which function is based on the bending of a bimaterial beam upon absorption of infrared energy. SiNx is explicitly chosen as the absorption material, isolation material as well as one of the actuation materials for multiple reasons. On the other hand, Al has been chosen as the bimaterial pair due to its larger mismatch in coefficient of thermal expansion (CTE) with the SiNx. Summarily, both SiNx and Al have primary importance in applications of cantilever-based microbolometers; the mechanical properties of these two materials are of paramount importance in determining the performance of microbolometers. In this work, SiNx was deposited with plasma-enhanced chemical vapor deposition (PECVD) at 300°C and Al with ebeam evaporation at room temperature. The purpose of this study is to examine the mechanical response of both PECVD SiNx and Ebeam Al films to thermal cyclings so as to predict their thermal-mechanical behavior for cantilever-based microbolometer applications. A commercial curvature measurement system (Tencor FLX-2320) was used to deduce residual stresses. The thermal cycling experiment started with three thermal cyclings from room temperature to 150°C, with a two-hour annealing at the peak temperature. Such experiment was followed by another three thermal cyclings from room temperature to a peak temperature of 300°C. It was observed that both SiNx and Al films have nonlinear behavior during the first thermal cycling. During the subsequent cyclings, however, such hysteresis was much reduced. For the Al film, it was observed that: first, its CTE changed with thermal cycling (e.g., 23.1 ppm/m°C-1 after cycling at 150°C; 18.5 ppm/m°C-1 after cycling at 300°C); second, its residual stress at room temperature increased significantly from compressive (about -200MPa) to tensile (about 300MPa) after completion of the aforementioned thermal cycling experiment; and third, the Al film underwent an unnegligible stress change when held at the peak temperature of 150°C for 2 hours (from about -280MPa to -100MPa). SiNx film was found to have a similar behavior in CTE and residual stresses, although its change in CTE was not as obvious as that of Al. The causes of instability in both SiNx and Al films were discussed in order to lead to promising processing paths for enhanced stability control and, ultimately, improved predictive capability for microbolometer performance.

SESSION U11: Poster Session: Metal and Polymer Thin

Films

Thursday Evening, December 2, 2004

8:00 PM

Exhibition Hall D (Hynes)

U11.1

Deformability of Thin Metal Films on Polymer Substrates. Teng Li¹, Zhenyu Huang¹, Zhigang Suo¹, Stephanie P. Lacour² and Sigurd Wagner²; ¹Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; ²Department of Electrical Engineering, Princeton University, Princeton, New Jersey.

Many flexible electronic devices comprise inorganic thin films (e.g., metals, transparent conductors and amorphous silicon) on organic polymer substrates (e.g., polyimide and silicone). When stretched or bent, the compliant substrate deforms, but the stiff films may crack or debond. Mechanical failure poses a significant challenge in the development of flexible and stretchable electronics. We study the deformability of metal films on polymer substrates. Recent experiments show that, when stretched, polymer-supported metal films rupture at strains larger than those reported for free-standing thin metal films. We use a finite element code to simulate the rupture process of metal films. A free-standing metal film ruptures by forming a single neck. By contrast, a metal film on an elastomer substrate may develop an array of necks before rupture. While these pre-rupture necks do not change the electrical conductance appreciably, they elongate the metal film, leading to a large overall rupture strain. If the metal film is bonded to a polyimide substrate, the substrate suppresses large local elongation in the film, so that the metal film may deform uniformly to very large strain. Combined with recent design concepts such as zigzag interconnects, thin metal films may be stretched even more. These stretchable interconnects are promising for applications in biological systems and severe dynamic environments.

U11.2

Microstructure evolution across interfaces of heterogeneous metal systems under ultrasonic impact. Youhong Li¹, Yinon

Ashkenazy² and Robert S. Averback³; ¹Computational Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Racah Institute of Physics, Hebrew University of Jerusalem, Urbana, Illinois; ³Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Nano-scale materials for electronic devices usually involve using multi-layers of dissimilar metals to obtain desired compatibility and performance. The mechanical stability of such structures is crucial to ensure that devices function properly. In this work, large-scale Molecular Dynamics (MD) studies have been performed on heterogeneous metal systems to investigate the microstructure evolution when shock waves propagate across interfaces between dissimilar metals. The effect of interfacial defects in the form of vacancies is evaluated.

U11.3

Localized Vibrational Modes in Metallic Nanocrystalline

Interfaces. Peter M. Derlet, Steven Van Petegem and Helena Van Swygenhoven; ASQ/NUM, Paul Scherrer Institute, PSI-Villigen, Switzerland.

The high frequency phonon properties of a computer generated nanocrystalline (nc) fcc Ni are investigated by directly calculating the onsite phonon Greens function using a recursion technique based on a continued fraction representation. It is found that the high frequency tail, observed in both experiment and previous simulation work, arises primarily from localized vibrational modes forming within the nc grain boundary regions (Phys. Rev. Lett. 92 (2004)). The location of such modes is found to correlate well with free volume within the grain boundary that has been identified by theoretical positron lifetime calculations. The relationship between such anomalous vibrational modes and atomic activity within the grain boundary will be discussed in the context of nanocrystalline plastic deformation mechanisms.

U11.4

Effect of Copper Thin Film at Ni-Ag Interface on Reactive

Solid State Dewetting. Nihed Chaabane, Lelia Mignot, Sylvie Poissonnet and George Martin; CEA-Saclay, SRMP, Gif sur Yvette, France.

Thick Ag films deposited onto polycrystalline Ni substrates, dewet the substrate when annealed at high temperatures in an oxygen atmosphere. Dewetting occurs when a nickel oxide layer is formed at the silver-nickel interface as a consequence of oxygen diffusion through the silver film [1-2]. Here, we show that a thin copper layer (10 - 15

equivalent monolayers) deposited at the Ni-Ag interface partially inhibit this reactive dewetting by changing the oxidation process. Scanning Electron Microscopy (SEM) observations of the non-dewetted regions reveal that the size of the recrystallized Ag grains is larger than in the rest of the sample. The remaining holes are especially concentrated at Ag grain boundaries and triple junctions. Microstructural analysis of the sample cross sections by Focused Ion Beam (FIB) show that in the non-dewetted regions the oxide is composed of a wide central duplex structure (a layer of equiaxed crystals near the Ni-oxide interface plus a columnar layer) some 4 microns thick followed by a thin layer, some tenths of a micron thick which forms a very flat interface with the Ag film. We have not observed any cavity nucleation in these regions. Cavity nucleation is the main identified mechanism of dewetting [2] for Ni-Ag samples. These observations are correlated to the presence of the thin Cu layer. Indeed glow discharge mass spectrometric measurements confirm the presence of a significant Cu peak at the Ag-oxide interface and a sharp one at the oxide-Ni interface with a small amount of Cu present throughout the nickel-oxide layer, i.e; the deposited Cu layer on Ni substrate diffuses toward the Ag-oxide interface during the oxidation process. The oxidation mechanisms and their influence on reactive solid state dewetting are discussed. [1] L. Mignot, P.J.A Mata, S. Poissonnet, and G. Martin, Phil. Mag. Lett. 80, 33 (2000). [2] H. De Monestrol, L. Mignot, S. Poissonnet, Ch. Lebourgeois, and G. Martin, Interface Sci. 11, 379 (2003).

U11.5

Anodization of Isolated Nanoscale Aluminum on Si and the Effects on Pore Growth. Patrick James Griffin, Robert W. Carpick and Donald S. Stone; Materials Science, University of Wisconsin-Madison, Madison, Wisconsin.

Anodic alumina has long been considered a viable material for templated growth of nanomaterials for electronic, magnetic and optical devices due to the ability to form self-organized nanochannels. Nano and micro dimension porous alumina integrated with Si substrates shows advantages over bulk films by presenting small, addressable pore regions for potential sensor applications. However, there has been little to no investigation into the effect of constraining the aluminum dimensions on the nanometer scale and the subsequent effects on pore growth. We have used electron beam lithography to pattern isolated aluminum regions on Si from 100 nm to several microns in size. To successfully anodize these small dimension aluminum areas the issue of carrying current to the aluminum islands must be overcome. We have studied the anodization of these aluminum regions on silicon via both the use of continuous aluminum networks and through the use of highly doped silicon substrates. The synthesis and characterization of these systems will be presented.

U11.6

Suppression of Dewetting in Pulsed Laser Melting of Thin Metallic Films on SiO₂. 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 integration of metallic thin films in advanced device applications. These include copper-based microelectronic interconnect technology facing formidable new limits associated with frequency and reliability as line widths are reduced, as well as the need for specialized electrode attachments to oxides in acoustic wave devices, MEMS and sensors. Post-deposition melting of metal films by pulsed laser irradiation is a promising route to obtain engineered microstructures and to control the distribution of alloying elements, phases, and precipitates in these applications. Unfortunately, dewetting of molten metal films is a problem that has long been observed on SiO₂, as well as other substrates. Dewetting on the nanosecond timescales corresponding to excimer laser melting the situation is less clear, but in general most metals appear to undergo a dewetting process that can often include hole formation and agglomeration of films into droplets. In this work, we show that by encapsulation with an over-layer of SiO₂, control of irradiated spot size, fluence, and attention to gas incorporation, metal films 100-200nm thick can be completely melted and resolidified on SiO₂ substrates without dewetting. Results are presented for the elemental systems Ni, Au, Cu, and Cr, along with a discussion of issues relating to nanosecond timescale melting, dewetting, and disruption of oxide-encapsulated films.

U11.7

Morphological and Stress Evolution During Thin Film Electrochemical Deposition. Tianzhi Luo, Donglei Fan and Robert Charles Cammarata; Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

The evolution of the morphology and intrinsic stress during electrochemical deposition of thin films will be presented. The in situ stress behavior was monitored using a sensitive wafer curvature

measuring system, and scanning electron and atomic force microscopy were used to characterize the thin film morphology. The systems studied include copper, nickel, silver, and bismuth. Unlike the case of evaporated metallic films which deposit by island growth, where the stress evolution for many systems was very similar, the electrodeposited films displayed a wide variety of behaviors depending on the system and the deposition conditions. The stress was correlated with morphological evolution, and resulted in both tensile and compressive behaviors. Morphological parameters that had a strong influence on the stress include island and grain size as well as surface roughness. In the case of bismuth, films often deposited with a microporous morphology that appeared to be the controlling parameter for the intrinsic stress. As in the case of evaporated films, there was a substantial stress relaxation when deposition was halted, although, in contrast to evaporated films, the relaxations were of either sign. The relation of the intrinsic stress to the film morphology during deposition for the different systems will be presented and compared to recently proposed models for island grown films.

U11.8

Stress Reduction in Tungsten Films Using Nanostructured Compliant Layers. Tansel Karabacak¹, Catalin R. Picu², Gwo-Ching Wang¹ and Toh-Ming Lu¹; ¹Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York; ²Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We present a new strategy for stress reduction in sputter deposited films by using a nano-structured compliant layer obtained either by an oblique angle deposition technique or by a high working-gas pressure process prior to the deposition of the denser continuous film. The technique is all in-situ, does not require any lithography steps, and the nanostructured layer is made from the same material as the deposited thin film. By using this approach we were able to reduce stress values by approximately one order of magnitude in sputter deposited tungsten films. These lower stress thin films also exhibit stronger adhesion to the substrate, which retards delamination buckling. This technique allows the growth of much thicker films and has enhanced structural stability. A model is developed to explain the stress relief mechanism and the stronger adhesion associated with the presence of the nanostructured compliant layer. This work is supported by the NSF.

U11.9

Patterning in CoxCu(1-x) Alloys under Ion Irradiation. Pavel Krasnochtchekov, P. Bellon and R. S. Averback; MATSE, University of Illinois at UC, Urbana, Illinois.

Phase separation behavior in thin CoxCu1-x films with various Co content (x = 10%, 15%, 20%) irradiated with 1.8 MeV Kr ions at different temperatures has been systematically studied. Development of phase separation in irradiated films (estimates of the size of Co precipitates and concentration of Co in solution) was monitored with the use of magnetic measurements. Analysis of magnetization data in the framework of superparamagnetic theory revealed that at irradiation temperatures T_i below T_i = 350 C, phase separation in CuCo films of all compositions stabilizes at high doses (by 5x10¹⁵ ions/cm²), indicating the existence of temperature-dependent steady states for these alloys under irradiation. At temperatures higher than 350 C, macroscopic-like coarsening is observed. At low temperatures (room temperature and below), FC/ZFC (field cooled / zero field cooled) measurements clearly show the randomizing effect of irradiation, as evidenced by the lowering of the point of divergence between the FC and ZFC curves. However, magnetization of films irradiated even at the lowest studied temperature (liquid nitrogen) does not completely vanish at high doses. The observed phase separation behavior of CuCo system under irradiation fits well with the predictions of the theoretical model for immiscible alloy films under irradiation (Phys.Rev.Lett. 84 (2000) 2885).

U11.10

Molecular-Dynamics Study of Ductile Void Growth Mechanisms in Metallic Thin Films. M. Rauf Gungor and Dimitrios Maroudas; Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts.

Understanding strain relaxation due to ductile void growth is important in order to establish a micro-scale plasticity theory for metallic thin films. It is also a topic of major technological interest for the reliability of metallic interconnects in microelectronic devices. Toward these goals, atomic-scale modeling based on molecular-dynamics (MD) simulation provides a powerful means for analysis of plastic deformation mechanisms and development of constitutive equations for continuum modeling of metallic thin-film mechanical behavior and stability. In this presentation, we report a comprehensive analysis of plastic deformation and ductile void growth mechanisms under biaxial tensile strain in Cu thin films with

cylindrical voids normal to the film plane and extending across the film thickness along the [111] crystallographic direction. Our computational analysis is based on isothermal-isostrain MD simulations within an embedded-atom-method parameterization for Cu and using slab supercells that contain millions of atoms. We present results for the evolution of the void volume and surface morphology, which were monitored to examine void growth and faceting. Elastic-to-plastic deformation transitions accompanied by dislocation emission from the void surface and surface morphological transitions, dislocation jogging, vacancy generation by jogged dislocations, dislocation-vacancy interactions, as well as nucleation and propagation of threading dislocation loops are analyzed in detail. In addition, the evolution of the dislocation population, stress field, atomic mobility, and dislocation motion were monitored systematically. Over a broad range of biaxial strain levels, the MD simulations reveal both fully elastic (under low strain) and elastoplastic deformation mechanisms that mediate void growth in the Cu thin film. At strain levels higher than the yield strain, void growth is 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. Our simulations show that vacancy generation, dislocation-vacancy interactions, and threading dislocation formation and motion are particularly important mechanisms at later stages of deformation (under high strain). The results contribute to our fundamental understanding of strain relaxation in metallic thin films through growth and morphological evolution of voids. They also contribute to a first-principles development of constitutive theories for the deformation behavior of such metallic systems.

U11.11
Temperature Dependence of Stress Distribution in Depth for Al and Cu Thin Films. Shinji Takayama, Tokuji Himuro, Yasushi Nakajima and Makoto Oikawa; Systems and Control Engineering, Hosei University, Tokyo, Japan.

The thermal stability of Al and Cu films, which are commonly used as an interconnect line in advanced ultra large scale integrated (ULSI) circuits, is an important reliability issue of ULSI semiconductor devices. To clarify this, we investigated their temperature dependence of stress distribution in depth by employing a grazing incidence X-ray scattering (GIXS) method. In this scattering geometry used at present study, the X-ray beam is incident on the surface at a very small grazing angle. The scattered X-rays are detected in the direction parallel to the film surface along a circle at constant distance from the sample. We realized, however, that in this geometry, the larger the incident angle became to get the X-ray depth profiling in thin films, the more the true scattering angle was underestimated. Thus, the rigorous correction should be made to get a true scattering angle. We have calculated these error correction factors and demonstrated it by using a Si(100) substrate. In this report, these error corrections were made for all measurements of depth stress distribution in thin films. It was revealed that the internal stress of (111) grains parallel to the cross-section of the as-deposited Cu film decreased lineally from the film/substrate interface and then tended to saturate near the free surface. On the other hand, that of (220) grains for Al films decreased with a slope lower than the Cu films toward the free surface. These stress distribution profiles, on the whole, were nearly unchanged on annealing except at the temperature that a large stress relaxation and a grain growth occurred. For Cu films, visible thermal voids started to grow when a large grain growth and stress relaxation took place, whereas for Al films, hillocks and whiskers appeared at 100°C depending on the film thickness. It was also realized that for Al films, population of hillocks increased with increase of the thickness, while for Cu films, the void population tended to decrease with increase of the thickness. Such thermal stability of Al and Cu films can be explained by the diffusional creep in thin films.

U11.12
Micromechanical Modeling for Thermo-Mechanical Reliability of Interconnects. Alberto Cuitino¹, Marisol Koslowski², Michael Ortiz³, Daniel Pantuso⁴ and Sadasivan Shankar⁴; ¹Dept. of Mech. and Aerosp. Eng., Rutgers University, Piscataway, New Jersey; ²Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico; ³Calci, Caltech, Pasadena, California; ⁴Intel Corp., Hillsboro, Oregon.

Due to increasing demand in electrical performance, new materials are developed and integrated for future generations of interconnect systems. As a result, uncertainty about structural integrity and possible failure mechanisms becomes a key concern during the circuit interconnect process development phase. Hence, having predictive and accurate thermo-mechanical models are very desirable in order to know in advance possible failure mechanisms, fundamentally understand them and find appropriate and optimal solutions. Thermo-mechanical related failures in interconnect lines occur as a result of a combination of different physical phenomena that are not well understood. These include mechanical, thermal and diffusion

mechanisms. Furthermore, material characterization of very thin films is often restricted due to limitations of experimental techniques to measure key material properties. In particular, interconnect materials that exhibit plastic deformation is not well characterized beyond the elastic limit. In order to understand the impact of each of the different phenomena involved, detailed coupled micromechanical models are needed to predict basic material behavior such as dislocation motion and multiplication, multislip, latent hardening and thermally induced softening, grain and surface diffusion mechanisms. A key outcome of the models will be the capability to predict the rate of vacancy generation and correlate it to microdefect formation and initiation (blistering, flaking and stress voiding). In this paper we focus on thermo-mechanical related phenomena from a micro-mechanics point of view. The main thrust is the prediction of micro-defect formation and their evolution driven by thermal and mechanical sources. In particular, we consider the void-nucleating mechanism of vacancy condensation and the subsequent growth by diffusion as the main source of micro-defect formation. Full-field numerical predictions of the evolution of the deformation and stress patterns driven by a homogeneous temperature reduction are presented. The simulations, which are conducted in representative 3D interconnect configurations, also provide the location, the critical size and the characteristic time of formation of potential micro defects.

U11.13
In-situ TEM Study of Dislocation Mechanisms in Nanoscale Cu Interconnects. Jin Ho An and Paulo Ferreira; Materials Science and Engineering Program, University of Texas at Austin, Austin, Texas.

The scientific and industrial requirements for high-load workstations and the public demand for fast personal computers have lead the semiconductor industry to produce more powerful microelectronic devices, mainly by increasing the device speeds. In order to achieve this goal, it is crucial to continue decreasing Cu interconnect widths. However, as downscaling of Cu interconnect widths progresses, thermal stresses during processing have become a reliability issue of concern to the microelectronic industry. This is due primarily to the fact that for the small grain sizes and distinct textures exhibited by submicron/nano Cu interconnect widths, the deformation mechanisms are expected to fundamentally change. To address these changes, in this study, the microstructure of 1.8 micron and 180 nm wide Cu interconnects, in particular their defect structure, was investigated through Transmission Electron Microscopy (TEM). In-situ TEM heating was also performed in order to observe the different dislocation dynamics exhibited by the Cu interconnects under thermal stress. In-situ TEM observations showed that dislocation motion is less pronounced in case of the 180nm Cu lines. In the case of 1.8 micron Cu lines, grain boundaries seemed to act as dislocation sources. Such different deformation mechanisms are expected to have an impact on the thermal behavior of Cu interconnects as downscaling of these interconnects continues.

U11.14
Electroless Gold Nanoparticle Film Deposition on III-V Semiconductor Surfaces. Hyuneui Lim¹, Byung-Oh Choi¹, Kwang-Young Kim¹, Carlo Carraro² and Roya Maboudian²; ¹Dept. of Advanced Industrial Technology, Korea Institute of Machinery and Material, Daejeon, South Korea; ²Dept. of Chemical Engineering, University of California at Berkeley, Berkeley, California.

We demonstrate the gold nanoparticle films prepared as a result of the immersion of InP, GaAs, and InSb substrates into dilute aqueous solution of AuCl₄⁻. Deposition proceeds via galvanic displacement in the absence of acid, pH adjusters, external reducing agents. The controlled depositions of nanoparticles are performed by modulation of plating parameters such as concentration, temperature, and immersion time. The deposition rate and surface morphology depend on the plating parameters as well as underlying semiconductor substrate. Deposited gold films exhibit excellent adhesion to GaAs and InSb surfaces but not to InP, independent of the plating time. The physical and chemical properties of gold-semiconductor interface are characterized by a variety of techniques, including x-ray photoelectron spectroscopy, atomic force microscopy, and electron microscopy. The feasibility of this reaction can be expected by simple redox potential calculation. This manner of deposition serves as a cost-effective, high-throughput method with potential applications such as high resolution patterning, interconnects, and metallization of MEMS devices.

U11.15
Materials Processing Under Repeated Pulse Laser Melting. Bryan Gundrum¹, Robert Averbach², Pascal Bellon² and Pavel Krasnochtchekov²; ¹Mechanical Engineering, University of Illinois Urbana Champaign, Urbana, Illinois; ²Materials Science and Engineering, University of Illinois Urbana Champaign, Urbana, Illinois.

Repeated laser pulse melting of copper/silver multilayers and co-deposited silver/cobalt thin films has been performed to explore nanoscale patterning. In order to achieve patterning the system dynamics must satisfy three requirements; most importantly competing dynamics must be present, the dynamics must be of similar strength, and the dynamics must operate on different length scales. In these experiments the copper/silver system was chosen due to it being immiscible in the solid and miscible in the liquid phase, thus setting up the competing dynamics when the system is cycled between the two states, it is the difference in the diffusion lengths for the solid and liquid that provides the different length scales, and finally the strength of the mixing and phase separation are of similar magnitudes. The silver/cobalt system, having no restoring dynamics due to it being almost completely immiscible in both the solid and liquid states allows us to investigate diffusion limited aggregation of the solid cobalt particles in liquid silver. Utilizing a 7ns Nd-YAG laser operating at 532nm, and a silicon substrate, cooling rates of 1011K/s were measured via time resolved reflectivity. The composition and microstructure were systematically investigated with cross-sectional and plane view TEM, and STEM, in addition to RBS and XRD. Experimental results are compared with computer simulations.

U11.16
Effect of Nanoscopic Fillers on the Viscoelastic Response of Polymers. Jean Harry Xavier¹, Miriam Rafailovich¹, Jonathan Sokolov¹, Young-Soo Seo¹ and Abraham Ulman²; ¹Materials Science, Stony Brook University, Stony Brook, New York; ²Chemical Engineering/Chemistry, Polytechnic University, Brooklyn, New York.

We have used a technique developed by Brochard (Macromolecules, 2004, 37, 1470) using free standing thin films to measure the viscoelastic response of filled polymer films. Transmission Electron Microscopy (TEM) experiments reported that fillers were well distributed within the films, and therefore no clustering and interfacial segregation occurred. Results from Shear Modulation Force Microscopy (SMFM) measurements revealed that the glass transition temperature of the polymer (T_g) was depressed by 10C relative to the bulk for Au (10 nm), and bulk like for Au (3 nm) and cloisite clay. The effects of nanoscopic fillers on the tracer diffusion coefficient were studied using neutron reflectivity (NR) and secondary ion mass spectrometry (SIMS). Both techniques, NR and SIMS, found that the diffusion coefficient was increased significantly for the Au 10 nm, and constant for the Au 3 nm and cloisite 6 clay. Values for zero shear rate viscosity extracted from the diffusion coefficient were compared to the shear strain calculated from the hole growth measurements, and theoretical predictions. Results were attributed to an increase in excluded volume when large particles were introduced into the matrix.

U11.17
Structural Evolution and Alignment of Cylinder-Forming PS-PEP Thin Films in Confinement Studied via Time-Lapse Atomic Force Microscopy. Qin Zheng and Steven J. Sibener; The James Franck Institute and Department of Chemistry, University of Chicago, Chicago, Illinois.

The generation of nanostructures having controlled orientation and a high degree of structural perfection has attracted significant attention due to many potential technical applications. Previous studies from our group have focused on details of defect dynamics in thin polymer films [1] and the utilization of templated grating substrates to produce essentially defect-free diblock copolymer "nanowires" by combining "top-down" and "bottom-up" assembly techniques [2,3]. Thin films of cylinder-forming polystyrene-*block*-poly(ethylene-*alt*-propylene) were spin-cast on patterned substrates. Thermal annealing at carefully selected temperatures drives the confined system into a lower energy state in which cylinder aligns parallel to the grating, due to interactions with the edge of the channel wall. Early observations have also demonstrated the aligned polymer nanostructures are relatively compliant to lithographic imprecision, accommodating ca. 10% deviation from the ideal channel dimension for a given number of confined cylinders. This accommodation works via compression and expansion in polymer dimension referenced to those at equilibrium in unconfined geometries. However, these previous AFM investigations required repeated cycles of imaging followed by *ex-situ* thermal annealing. Moreover, they only gave glimpses of the details of the competing kinetic and thermodynamic processes which drove the time-evolution of the system. To address these concerns, we have now moved to *in-situ* studies utilizing high-temperature AFM (HT-AFM) which allows us to map out such processes during annealing. Such time-lapse observations of defect evolution at a given temperature allow us to examine the dynamics of polymer microdomain coarsening, while studies at different temperatures help us understand the energetics for other processes. We focus on the mechanistic details which govern defect evolution in confined copolymer thin films. Another aspect of this presentation is to explore in detail polymer compliance in

confinement. This phenomenon has been studied previously for symmetric diblock copolymers [4], with less focus on asymmetric systems. We have lithographically fabricated tapered nanochannels of various tapering angle, giving a direct route to examining polymer structure as a function of changing confinement. Upon annealing, alignment is established along the channel direction. Early indications suggest that polymer films align more readily in channels with larger tapering angles. Furthermore, HT-AFM gives clear snapshots of how the system evolves from its initially random state towards structural perfection. [1] J. Hahn, S. J. Sibener, *J.Chem.Phys.* **114**, 4730 (2001). [2] D. Sundrani, S. B. Darling, S. J. Sibener, *NanoLetters* **4**, 273 (2004). [3] D. Sundrani, S. B. Darling, S. J. Sibener, *Langmuir* **20**, 5091 (2004). [4] P. Lambooy, T. P. Russell, G. J. Kellogg, A. M. Mayes, P. D. Gallagher, S. K. Satija, *Phys.Rev.Lett.* **72**, 2899 (1994).

U11.18
Abstract Withdrawn

U11.19
Stress Evolution in PMMA Spun Films. Anita M. Bowles and Frans Spaepen; Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts.

Stress evolution in organic films continues after the end of spin coating. At room temperature tensile stress development due to solvent evaporation competes with stress relaxation. The influence of molecular weight, spin speed, and thickness on these processes is explored for films of polymethyl methacrylate (PMMA) spin cast onto silicon substrates. Stress in the film is measured as a function of time in two perpendicular directions over a large area using a multiple laser beam system that detects the curvature of the substrate.

U11.20
Deformation of Lamellar Glassy/Rubbery/Glassy Triblock Copolymers - Oriented Films and Polycrystalline Structures: Micromechanical Models and Experimentation. Theodora Tzianetopoulou and Mary C. Boyce; Department of Mechanical Engineering, MIT, Cambridge, Massachusetts.

Styrenic block copolymers are among the most widely used polymeric materials today. Their applications span a wide range of industries, from automotive, footwear, wire and cable, to adhesive, sealant and medical. Owing to their wide range of nanostructural features, block copolymers have a potential for several novel nanotechnological applications. Our research is geared towards the development of predictive models, both for oriented and polycrystalline block copolymers, in order to guide in efficient material design and product development, from nano- up to macro scales. Micromechanically-based finite element models, in 2 and 3 dimensions, are used to investigate the relation between the microstructural evolution and the effective macroscopic mechanical behavior of oriented and multigrain styrene/butadiene/styrene lamellar triblock copolymers during deformation. The numerically calculated response to various loading conditions, including tension under ambient and elevated temperatures as well as nanoindentation, is compared to available experimental data, microscopy images and SAXS patterns from the literature in an effort to investigate most aspects of lamellar block copolymers' deformation micromechanics.

U11.21
Entropy Effect on the Melting Point Depression in the Ultra-thin Polymer Films. Yantian Wang¹, Shouren Ge¹, Miriam Rafailovich¹, Jonathan Sokolov¹ and Arnold Lustiger²; ¹Materials Science and Engineering, SUNY at Stony Brook, Stony Brook, New York; ²ExxonMobil Research and Engineering Company, Annandale, New Jersey.

The melting point of the thin and ultra-thin films of short chain branched polyethylene with different branching concentration was studied by the shear modulus force microscopy (SMFM) as a function of film thickness (10-40nm). Silicon, aluminum and polyimide substrates were used to rule out the pure geometric confinement effect on the T_m . The T_m was found to decrease with the film thickness decrease for the films on all the substrates. The largest T_m depression was observed in the ultra-thin film of the highest branching concentration on the silicon substrate, which was 38oC lower than the bulk value. As the transmission electron microscopy (TEM) and Fourier transformed infrared spectroscopy (FTIR) results showed no decrease in the degree of crystallinity in the ultra-thin film, the entropy effect was regarded as the main cause for the large T_m depression. The interfacial energy and the branching concentration play an important role in the melting entropy of the ultra-thin films on the solid substrates, the large T_m depression was attributed to an increased melting entropy.

8:30 AM U12.1

Viscosimetry of Polymer Thin Films at Attractive Surfaces.

Chunhua Li¹, Clive Li¹, Tadanori Koga¹, Young-Soo Seo², Yuan Sun¹, Sarika Sharma¹, Larry Lurio³, Shira Billet⁴, Miriam Rafailovich¹ and Jonathan Sokolov¹; ¹Material Science, State University of New York at Stony Brook, Stony Brook, New York; ²NG-7, National Institute of Standards and Technology, Gaithersburg, Maryland; ³Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois; ⁴Stella K Abraham High School, Hewlett, New York.

We demonstrate that the viscosity of a polymer film can be measured in situ by observing the liquid-liquid dewetting of polymer bilayer films. The viscosity, as deduced from the dewetting velocity [1], was in good agreement with the bulk value [2], and the viscosity measured by using the complementary technique X-ray Photon Correlation Spectroscopy (XPCS) [3]. In order to determine whether we are observing shear induced effects, we also compared the viscosity with that obtained from Secondary Ion Mass Spectroscopy (SIMS) and Neutron Reflectivity (NR) diffusion measurements where the diffusion coefficient is related to the Stokes Einstein relation inversely proportional to the viscosity. We then use the technique to systemically investigate the effect of film thickness and surface interactions on the effective viscosity of polymer thin films. We found that the effective viscosity increases dramatically with decreasing the film thickness. We attribute this to the pinning of the polymer chains at the polymer/Silicon interface. To further test this theory, we first spun cast a PS layer that was smaller than the radius of gyration. The layer was then annealed so that strong bonding could occur with Si substrate. Samples prepared in this manner had lower viscosity than those prepared in single layer directly in contact with the substrate. This behavior confirmed the "two-fluid theory". Another consequence of the surface interactions are large regions beneath the probe layer where melt fracture is observed. We show that these features arise from shear in the film when the shear rate due to dewetting is larger than the reptation time. [1] Brochard-Wyart, F., Langmuir 9, 3682 (1993) [2] D.J.Plazek, V.M.O'Rourke, J. Polym.Sci. Part A-2, 9, 209 (1971) [3] Hyunjung Kim, Phys.Rev.Lett. 90 (6), 068302 (2003)
Supported in part by the NSF-MRSEC

8:45 AM U12.2

Thermal Expansion and Deformation in Polymer

Nanostructures. Ronald L. Jones¹, Christopher L. Soles¹, Ron M. Reano², Stella W. Pang², Eric K. Lin¹, Wen-li Wu¹ and Diego M. Casa³; ¹NIST Polymers Division, Gaithersburg, Maryland; ²Dept. of Elec. Eng. and Comp. Sci., University of Michigan, Ann Arbor, Michigan; ³CMC-CAT, Adv. Photon Source, Argonne National Laboratory, Argonne, Illinois.

An extensive body of work on polymer thin films has revealed significant deviations from bulk properties in polymer thin films when the film thickness approaches the molecular dimensions. The source of these deviations can be either confinement of the molecules into non-bulklike conformations or the increased relative importance of surface effects such as a reduced density or Hamaker-like long range interactions. Based on these explanations, we expect even more dramatic deviations in polymer nanostructures where the system is confined along multiple dimensions, and the surface to volume ratio is significantly increased. Examination of nanostructures, however, has been limited due to the complicated boundary conditions of multiple surfaces, small sample volumes, and lack of fabrication methods. Recent developments in nanoimprint lithography have allowed the production of model nanostructure samples. Using small angle x-ray diffraction, we have examined the deformation behavior of polymer nanostructures created using nanoimprint lithography as a function of thermal annealing. The nanostructures are in the form of line gratings that float on an essentially infinitely thick polymer substrate, where the substrate is of the same material as the nanostructure. In this limit, the substrate-nanostructure interactions are well defined and the final equilibrium state is defined as state of complete wetting. The structures are therefore found to melt and deform onto the underlying substrate during heating above the glass transition temperature. The dynamic behavior of this equilibration is examined as a function of temperature and nanostructure size to elucidate deviations from bulk behavior. Experimental data is then compared to the extensive body of theoretical work on dynamic wetting.

9:00 AM *U12.3

Role of Physically Pinned Layers on the Wetting and Thermodynamics of Polymer Thin Films. Sanat Kumar, RPI, Troy, New York.

When a polymer melt is contacted with an attractive flat surface, chains that contact the surface are effectively pinned to it over macroscopic times. These pinned layers are autophobic overlayers thus dramatically altering the wetting properties of these substrates. These pinned layers also dramatically alter the thermodynamics of polymer blends in their vicinity. We assess the properties of such pinned layers through a judicious combination of theory and experiments on both thin polymer films and also polymers filled with nanoparticles.

9:30 AM U12.4

Self-assembled nanopatterns in a polymer thin film induced by an in-plane electric field. Wei Lu and David Salac; Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

This paper reports our experimental work and simulation on self-assembled morphological patterns in a thin polymer film induced by an in-plane electric field. The film was first spin-coated onto a glass wafer. Then it was heated to above its glass transition temperature to achieve mobility in the fluid. An in-plane electric field was applied using two parallel electrodes, spaced 10 mm apart, whereupon the initially flat polymer/air interface lost stability and formed islands. The self-assembled islands exhibited a narrow size distribution and demonstrated spatial ordering. We attribute the pattern formation to a combined mechanism of minimization of combined interface energy and electrostatic energy. We incorporate phase separation, mass diffusion and Navier Stokes equation into a phase field model. The simulation reveals remarkably rich dynamics and suggests a significant degree of experimental control. Diverse self-assembled patterns may be induced in a polymer thin film by electric field design or electrostatic template. These polymer patterns may be applied directly in functional devices, or serve as templates to pattern other materials.

10:15 AM U12.5

Critical Thickness Effects in Polystyrene Thin Films: Mechanical Behavior and Orientation Effects.

Manish Deopura¹, Bizhong Zhu², Dimi Katsoulis² and Frederick J. McGarry¹; ¹Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Advanced Technologies and Ventures Business R&D, Dow Corning Corporation, Midland, Michigan.

We have selected polystyrene, a widely used thermoplastic material, as a model polymer to demonstrate critical thickness concepts in thin film polymers. Although polystyrene is used widely in reinforced rubber forms such as HIPS, as a virgin material it is known to be brittle and undergoes brittle fracture with a maximum strain to failure of less than 3%. Based on theoretical models, it has been shown that when polymers are thinned below a critical dimension their maximum strain to failure value and hence the toughness increases. This critical thickness value can be attributed to the intrinsic deformation mechanisms of polymers, which begin to dominate toughness properties for thin films, whereas for bulk materials macroscopic deformation processes govern the toughness properties. In the present work thin polystyrene films on various substrates including stainless steel, silver and polysulfone have been investigated. We have demonstrated a brittle to ductile transition across the critical thickness value which is approximately 0.1-0.2 micron. To obtain this critical thickness value new tensile and flexural tests have been developed which allow us to measure and compare the toughness properties of thin vs. thick films. In order to determine strain to failure values for respective polystyrene films, the films have first been stretched to successively increasing strains and then optical microscopy has been performed on them. For thin films (< 0.1 micron) it is observed that the strain to failure increases substantially (>10%). In order to understand and compare orientation effects in thin vs. thick films, reflection FTIR studies have been carried out. Orientation results demonstrate that the amount of orientation in thicker films is much greater than thinner films. Reflection FTIR studies have also been used to determine the type of strain (elastic or plastic) which these thin films exhibit when stretched to extended to these large values.

10:30 AM *U12.6

Probing the Elastic Modulus of Ultra Thin Polymer Films.

Christopher M. Stafford, Bryan D. Vogt, Duangrut Julthongpipit and Michael J. Fasolka; Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

Emerging technologies such as MEMS, NEMS, nanoimprint lithography require an understanding of the physical and mechanical properties of materials in the ultra-thin regime (1 nm < h < 100 nm). Existing data attained from a variety of techniques such as nanoindentation, AFM, Brillouin light scattering, and surface acoustic wave spectroscopy display confounding views on the measured changes in material properties when confined to thin film geometries. We present a recent measurement platform that is particularly amenable to the measurement of the mechanical properties of

ultra-thin films. This method exploits a buckling instability that arises when a compressive strain is applied to a bilayer system consisting of a stiff coating (specimen) adhered to a relatively soft elastic substrate, where the specimen modulus is measured through the buckling wavelength. We apply this technique towards a model system comprised of polystyrene (PS) with a molecular weight range above and below the entanglement molecular weight. For the thinnest films, we observe an order of magnitude decrease in modulus. We will discuss several arguments for the observed decrease in film modulus in the ultra-thin regime.

11:00 AM U12.7

Morphological instability and kinetics of a compressed elastic film on a viscoelastic substrate. Rui Huang and Se Hyuk Im; University of Texas at Austin, Austin, Texas.

Several techniques have been developed recently to fabricate ordered structures at micro- and nano-scales with thin films wrinkling on compliant substrates. On an elastic substrate, equilibrium and energetics set the critical condition and select the wrinkle wavelength and amplitude. On a viscous substrate, wrinkle grows over time and the kinetics selects the fastest growing wavelength. More generally, on a viscoelastic substrate, both energetics and kinetics play important roles in determining the critical condition, the growth rate, and the selected wavelength. This paper studies the wrinkling process of an elastic film on a viscoelastic substrate, extending and unifying previous studies for elastic and viscous substrates. The film is elastic and modeled by nonlinear von Karman plate theory. The substrate is linear viscoelastic with a relaxation modulus typical of a cross-linked polymer. A classification of the wrinkling behavior is made based on the critical conditions at the elastic limits, the glassy and rubbery states of the viscoelastic substrates. A critical compressive stress exists, below which a flat film is stable. Linear perturbation analyses are conducted to reveal the kinetics of wrinkling subjected to intermediate and large compressive stresses. Depending on the stress level, the growth of wrinkle at the initial stage can be exponential, accelerating, linear, or decelerating. In all cases, the wrinkle amplitude saturates at an equilibrium state after a long time. Subsequently, both amplitude and wavelength of the wrinkle evolves, but the process is kinetically constrained and slow compared to the initial growth. Numerical simulations of evolving wrinkles are conducted and compared to experiments.

11:15 AM U12.8

Evolution of Wrinkle Patterns in a Thin Solid Film on a Liquid. Wei Hong, Zhenyu Huang and Zhigang Suo; DEAS, Harvard University, Cambridge, Massachusetts.

Experimental observations have accumulated in recent years that solid films on liquid substrates can form intricate wrinkle patterns. We report on a model that evolves a full field of wrinkles. A thin solid film on a liquid substrate is under a compressive stress in the plane of the film. To relax the elastic energy, the film wrinkles. The liquid remains adhesive to the solid film, and flows to accommodate the elastic deformation of the film. The thin solid film is modeled by an elastic nonlinear plate theory. Depending on its thickness, the liquid is modeled either by the lubrication theory or as a semi-infinite viscous substrate. A spectral method is developed to simulate the evolving wrinkle patterns. The wrinkles first buckle up, with a nearly constant wavelength and exponential growing amplitude. Subsequently, the wrinkles coarsen in a self-similar manner, with the wavelength and the amplitude growing proportionally. We show the effect of the initial film stress and the liquid thickness on the wrinkle evolution.

11:30 AM U12.9

Nonlinear analyses of wrinkles in films on soft elastic substrates. Zhenyu Huang, Wei Hong and Zhigang Suo; Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts.

Subject to compression in its plane, a film on a soft substrate often wrinkles. This paper reports on nonlinear analyses of the wrinkles. For an array of stripe wrinkles, the elastic energy is a fourth order polynomial of the wrinkle amplitude, so that the wrinkle instability behaves similarly to a phase transition of the second kind. The flat film becomes wrinkled when the magnitude of the membrane force exceeds a critical value. We obtain the equilibrium wrinkle wavelength and amplitude by minimizing the elastic energy. A spectral method is developed to simulate two-dimensional wrinkle patterns. Depending on the anisotropy of the membrane forces, the wrinkle patterns can be stripes, labyrinths, or herringbones. Wrinkle patterns are also affected by the spatial distribution of the membrane forces. Statistical averages of the amplitude and wavelength of the random wrinkles correlate well with the analytical solution of the stripe wrinkles.

11:45 AM U12.10

Stretchability of complex patterns of thin metal conductors

on elastomeric skin. Stephanie P. Lacour and Sigurd Wagner; Electrical Engineering, Princeton University, Princeton, New Jersey.

Skin-like electronics will be multifunctional systems that perform electrically actuated functions and conform to arbitrary surfaces. Their applications include bodysuit sensors, implantable medical devices and stretchable robotic skin. The skin is likely to be designed as an active matrix with electronic components placed on mechanically rigid subcircuit islands, which are interconnected with stretchable metallic conductors. We have previously shown that 25nm thick gold stripes on 1mm thick silicone membrane retain electrical conduction when stretched up to 60% along their long dimension. To function as electrical interconnects in integrated circuit skins, the metallization must be stretchable in arbitrary directions. Therefore we have made and tested the mechanical and electrical properties of complex conductor patterns including X and Y oriented lines, tee and cross junctions. We find that the metal patterns continue to conduct under uniaxial stretching (accompanied by perpendicular contraction) in the X or Y direction. We made a stretchable inverter circuit of thin film transistors, which relies on X and Y oriented interconnects. This circuit keeps operating when cycled through up to 12% of uniaxial stretching.