SYMPOSIUM U
Stability of Thin Films and Nanostructures
November 29 - December 3, 2004

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* Invited paper
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 for self-assembled quantum dots. The transition from planar growth to islands poses a longstanding puzzle in the understanding of the island formation process. 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 size of 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 are universal in shape and size, 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 steep domes to shallower pyramids, is a general phenomenon that can be controlled by lithographic patterning of the SOI prior to the deposition process. 

### 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) provides unique new phenomena. The essential thermodynamic instability of the very thin crystalline layer (called the template layer) resting on an oxide overlayer is responsible for the growth of InAs quantum dots on GaAs(100) obtained by scanning tunneling microscopy. The atomic-scale experiments demonstrate that the size and shape of 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 are universal in shape and size, 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 steep domes to shallower pyramids, is a general phenomenon that can be controlled by lithographic patterning of the SOI prior to the deposition process. 

### Microscopic View of InAs Quantum Dot Growth and Overgrowth on Patterned Substrates

Chao Qian, Max Planck 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, but they also are a platform for the design, fabrication and device integration of nanostructures. Both top-down and bottom-up methods have been developed for the handing of matter at the molecular and nanoscale level. 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 intensively studied for more than a decade and a number of important achievements have been obtained concerning their electronic and optical properties, a definitive 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 size of 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 are universal in shape and size, 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 steep domes to shallower pyramids, is a general phenomenon that can be controlled by lithographic patterning of the SOI prior to the deposition process.
that appear to be neither stable nor metastable according to a simple energetic analysis; free energy is reduced as islands translate in a confined direction relative to a two-dimensional post-deposition pattern; 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 is blocked by atomistic features requiring a 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. Our results reveal a novel island diffusion mechanism in which the substrate allows the growth of small 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. [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.

In-Situ Studies of Cu$_2$O Nano-Island Formation on Cu (001). Jeffrey A. Eastman, Paul H. Fauss, 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) SrTiO$_3$ substrates are oxidized to form crystallographically-aligned Cu$_2$O nano-islands on the Cu surface. By measuring oxygen uptake 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$_2$O/Cu 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 are observed. A transition from QD to QWR behavior along the stereographic substrate moving from (100) toward (311)A along the stereographic. We report on the effect of the orientation of a GaAs scanning tunneling microscopy (STM). For the same coverage of smaller than expected. Large reversible changes in the oxide lattice 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, this transition from QD to QWR behavior along the stereographic is observed as a function of the orientation of the substrate constraint is influencing the behavior. The prospects for engineering these constraints to influence nanopattern formation will be discussed.

Orientation dependence behavior of self-assembled (In,Ga)As quantum structures on GaAs substrates.

Shahrak Seydohamedeh, Zhihun 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 surface morphology along the (111)A, including (100) and (111)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 (311)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 (311)A surface is interpreted as observing a transition taking place from quantum dots to quantum wires on the (511)A surface. The observed 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.

Energetics of Trench Formation Around Ge/Si Quantum Dots. Diwangauly TulSiaram Tanbe and Vivek B. Shenyu; Solid Mechanics, Brown University, Providence, Rhode Island.

At high growth temperatures, the mid-facet 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 qualitative agreement with recent experimental observations.

SESSION U2/JJ12/KK2: Joint Session: Patternning and Steps on Surface

Chairs: Jim Evans and Vivek Shenyu

Monday Afternoon, November 29, 2004

11:30 AM U1.7/JJ11.7/KK1.7

1:30 PM U2.1/JJ12.1/KK2.1

1:30 PM U2.3/JJ12.3/KK2.3
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 Erlich-Schwoebel barriers, and nucleation. The problem is simplified in favorable cases, by faster than kinetic Monte Carlo. For growth near equilibrium we need to treat attachment-detachment from 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.

3:45 PM U2.5/J12.2/KK2.5
Formation of Ridges on Patterned Masers and Their Role in Evolution of Step Arrays on Masse. Yee-Chul Chang and Jack M. Bhukely; 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 on each terrace away from 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 nearest-neighbor interactions. This limit yields a nonlinear 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 continuum theory of 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 chirality-induced on a sufficiently fine grid. The results suggest that under conditions 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, the adatom is well localized on the lowermost terrace and that the upper terrace, the steps redistribute to form step density waves that change shape after a short time. With no Erlich-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/J12.3/KK2.5
Self-ordering of Nanoarrays on Vicinal Si(001) Surfaces and Its Application to Heterogeneous Nanostructures. Taka Tsuchida, Kazunori Terada, Tomoyuki Miyamoto, Masahiro Fujii and Huis Suen, H.Koizuma, Sapporo, Japan

Surface nanostructures by taking advantages of self-ordering or self-organization have been attracted much attention in nanofabrication of semiconductor device structures. Pecudically 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 (001) surfaces of the Si(001) surfaces 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 perpendicular anisotropy of the growth induced bands, 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 configuration on vicinal Si(001) surfaces after high temperature (1400 K) annealing and found that self-ordered nanofacets consisting of pairs of {0001} and {11-2n} facets, were generated. This study is much more delicate than the irreversible case. We will discuss the issues that arise, and how we deal with them.

4:15 PM U2.7/J12.7/KK2.7
The Controlled Self-Assembly of Nano-Structures by the Activated Stranski-Krastanow Transition Method. Cheng-hsin Chin, 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 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 use of the pattern of the SK film that is 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 control the size of 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 rings, 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 patterns causes 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, with three-dimensional numerical simulation that demonstrates the potential capability of the ASKT method.

4:30 PM U2.8/J12.8/KK2.8
Stability and Evolution of Nano-ripples on Crystalline Surfaces. Ashwin Ramachandran 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 Erlich-Schwoebel barrier at step-edges. This method is used to model recent experimental studies of relaxation of a Cu(001) surface. The relaxation includes processes 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, one wavelength, we observe that the decay behavior is not so that of a sinusoid of a single wavelength. The inherent nonlinearity of the evolution equations leads to significant changes in the modes in the vicinity of the dominant wavelength. Numerical calculations account for these coupling effects are in very good agreement with the experimental observations.

4:45 PM U2.9/J12.9/KK2.9
Dislocation Driven Surface Dynamics on Solids. Sundar V. Khera12, S. Kodambaka12, W. Siewk12, K. Ohmori12, M. Petrov12, E. Greene12, S. Kodambaka12, W. Siewk12, K., O., Petrov12, J. E. Greene12, W. Siewk12, K. Ohmori12, M. Petrov12, E. Greene12, S. Kodambaka12, W. Siewk12, K.

Using low-energy electron microscopy, we investigate the near-equilibrium dynamics of surface-terminated dislocations. Dislocations driven surface motions in materials, such as Si and GaAs, have been observed, both for device applications and for understanding of basic surface physics. Silicon carbide is an important compound semiconductor, which possesses perpendicular anisotropy of the growth induced bands, 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 configuration on vicinal Si(001) surfaces after high temperature (1400 K) annealing and found that self-ordered nanofacets consisting of pairs of {0001} and {11-2n} facets, were generated. This study is much more delicate than the irreversible case. We will discuss the issues that arise, and how we deal with them.
We find that $\omega$ is independent of the local environment and ambient, and decreases linearly with time. From the temperature-dependent $\omega$ data, we determine a phonon barrier of $4.2\pm 0.3$ eV for the growth of spirlars. 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.\textsuperscript{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.\textsuperscript{2} K. Kodambaka, S.V. Khare, W. Swiech, K. Ohmori, I. Petrov, and J.E. Greene, Nature \textbf{429}, 49 (2004).

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

\textbf{U3.1}

\textbf{High Frequency Phonon Modes in Nanoimprinted Gratings and Nanowires for Microelectronic Applications.}
Colm M. Flannery\textsuperscript{1,4}, Sudook Kim\textsuperscript{1}, Ward Johnson\textsuperscript{1}, Stephanie Hooker\textsuperscript{1}, Christopher Soles\textsuperscript{2}, Ryan Hartschuh\textsuperscript{3}, Alexandre Kisliuk\textsuperscript{3}, Mary K. Swiech, K. Ohmori, I. Petrov, and J.E. Greene, \textit{Nature} \textbf{429}, 49 (2004).

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 be 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-phonon 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 and 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 mechanical properties do 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.

\textbf{U3.2}

\textbf{The Evolution of Surface Roughness During Homoepitaxial Growth on Patterned GaAs(001)-the Length Scale Dependence and Temperature Dependence.}\textsuperscript{a}
Tabatha Joan Garrett\textsuperscript{1,2}, Tabassom Tadayon-Eslami\textsuperscript{1,2}, Hang-Chih Kao\textsuperscript{3} and Raymond J. Phaneuf\textsuperscript{4},\textsuperscript{1} Chemistry, North Carolina State University, Raleigh, North Carolina; \textsuperscript{2}Laboratory for Physical Sciences, University of Maryland, College Park, Maryland.

We investigate the evolution of the surface roughness on patterned GaAs (001) surfaces \textsuperscript{a} during homo-epitaxial growth at temperatures below and above the pre-roughening transition temperature (PRT) \textsuperscript{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 distance between the centers 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 that in the comparison of the evolution of the surface roughness, the parameters at temperatures both above and below the PRT. \textsuperscript{2} Work supported by the Laboratory for Physical Sciences and an MRSEC \textsuperscript{1} H.-C. Kan, \textit{et al.}, Phys. Rev. Lett. 92, 146101 (2004) \textsuperscript{2} V. P. LaBella, \textit{et al.}, Phys. Rev. Lett. 84, 4192 (2000).

\textbf{U3.3}

\textbf{Stress Stability of Poly-SiGe and Various Oxide Films in Humid Environments.}
Cagri W. Long\textsuperscript{1}, Brian L. Bircumshaw\textsuperscript{2}, Tatiana Dorofeeva\textsuperscript{1}, Belgis Solomon\textsuperscript{3}, Tsu-Jae King\textsuperscript{1} and Roger T. Howe\textsuperscript{1,2}, \textsuperscript{1}Electrical Engineering and Computer Sciences, University of California at Berkeley, Berkeley, California; \textsuperscript{2}Mechanical 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 possible a promising structural material for modular integration with electronics.\textsuperscript{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.\textsuperscript{2} Recent results show that the residual stress of poly-SiGe films is, in fact, stable in ambient conditions. Due to dielectric 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 becomes 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 400°C LPCVD oxide becomes more compressive over time while stresses of 1000°C dry and wet thermal oxides remain the same. The stresses of PECVD oxides deposited below 400°C also drift towards more compressive, but SiGe is more stable than the 400°C PECVD oxide. LPCVD low temperature oxide (LTO) films are known to be porous and of poor quality.\textsuperscript{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 \textsuperscript{2} is due to the instability of the LTO films. The backside LTO films became more compressive, causing an apparent positive drift in the SiGe film stresses. Stress drift dependent on SiGe concentration \textsuperscript{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 \textit{et al.}, \textit{J. MEMS}, 12, p. 160-171 (2003) \textsuperscript{2} B. Bircumshaw, et al., \textit{Tech. Digest of MEMS04}, p. 514-519 (2004) \textsuperscript{3} M. Madou, \textit{Fund. Of Microf.,} 2nd ed, CRC Press, p. 302 (2002) \textsuperscript{4} G. Stoney, \textit{Proc. Roy. Soc London}, A82, 172 (1909).

\textbf{U3.4}

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

Quasiparticle corrections to the electronic energies have been calculated for small GaP fullerenes, a new class of nano-scaled molecules recently predicted to be stable up to show sp2 like formation \textsuperscript{1}. These clusters have been also characterized by us for their optical absorption spectra using Time-Dependent Density Functional Theory \textsuperscript{2}. The comparison between single-particle and optical absorption spectra supports the presence of quasiparticles with binding energy up to 3 eV \textsuperscript{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 successful synthesis of such systems via optical absorption and quasiparticle spectra. \textsuperscript{1} V. Tazzini, F. Buda, A. Fasolino, Phys. Rev. Lett. 85, 4554 (2000) \textsuperscript{2} G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. 74, 801 (2002) \textsuperscript{3} G. Cappellini, F. Casula, J. Yang, F. Bechstedt, Phys. Rev. B 56, 3529 (1997).

\textbf{U3.5}

\textbf{The Role of Surface Step in Stabilizing Surface Structures.}
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 through their elastic interactions. The model is a continuum analog 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. Anti Kuronen, Laura Juvenon and Ville Lilja; Laboratory of Computational Engineering, Helsinki University of Technology, Espoo, Finland.

One of the most common defects 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 dislocations at low concentrations but are not present 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% 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 potential 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 importance 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 orientation of 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 500 strain. So far much effort has focused on investigating the shape of quantum dots, which are terminated by shallow (105) facets ("huts" [1]). At larger 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 280C etches Si1-xGe/xSi(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 used 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 lattice 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 Harinaruputran 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 phase as the substrate and B rich 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 dots (QDs) 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 facets. At high 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 contents of 20% or less are believed to go through 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 significant 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 heteroepitaxial dilute SiGe alloys on Si(100) [5]. Following the known “hut” and “dome” islands, a new “barb” shape is reached via a shape transformation, in which step (111) facets are introduced. After the initial formation of small [111] facets, the “barb” shape evolves via a nucleation and growth process. 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 - as compared to the limit of lattice mismatch strain. References: [1] Y.-W. Mo, D. E. Savage, B. S. Swartzentuber, and M. G. Lagally, Phys. Rev. Lett. 65, 1020 (1990).

9:00 AM U4.3
Formation of Ge/Si Nanostructures on the Atomic Level. Bert Voigtlander, Vasily Chepevano, Neelima Paul and Josef Myslivecek; Forschungszentrum Julich, Julich, Germany.
The step-flow growth mode is used to fabricate two-dimensional Si and Ge nanostructures with widths of 10 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 Si and Ge is occurring at a rate of 1.7 and 1.4 monolayers per minute, respectively.

9:15 AM U4.4
Kinetic Control of Dome Cluster Composition by Varying Ge Deposition Rate. Emily McDaniel1, Jeff Drucker1,2, P. A. Crozier2, Qian Jiang1 and David J. Smith1,2; 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 630°C is 30% larger than for Si(100) substrates. For substrate temperatures near 8 ML (1 ML = 6.78 x 1014 atoms/cm2) and deposition rates between 0.1 and 0.4 ML/min, higher deposition rates decreased the mean dome diameter and increased the dome area density. For growth at T=500°C, the mean dome diameter varied between 100 and 70 nm, and for T=550°C, between 55 and 111 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 in Ge content with deposition rate is the decrease in the pyramid-to-dome volume ratio 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=500°C with rates of 1.4 ML/min and 1.75 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). Siyuan Lu1, Anupam Madhukar1, Steven Hughes2 and A. Paul Alivisatos1; 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 on single crystal surfaces is attractive for 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 trioctyl 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 details of the stability were investigated utilizing 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, we observe strong 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) microstructures 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 NCQDs and the substrate.

10:30 AM U4.7
Semiconductor Nanocrystal Quantum Dots on Single Crystal Semiconductor Surfaces: Stability and Structure. Atul Kohkar1, S. Basu1, A. Madhukar1,2, S. Hughes2 and A. Paul Alivisatos1; 1Departments of Materials Science & Physics, University of Southern California, Los Angeles, California; 2Department of Chemistry, University of California, Berkeley, California.

Rebonded-Step (RS) reconstruction takes place at such facets, deeply rebounded-Step (RS) reconstruction takes place at such facets, deeply
Heteroepitaxial 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). 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 dewetted the Ru substrate by 3-D islands migrating "down" substrate steps. We have observed islands thicken by more than 50 nanometers in this way. This downhill-migration process allows 3-D growth to occur on islands that would not grow otherwise, 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 obstruct 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 Ag crystals on the substrate. Typical substrate steps have a width of 10-100 nm, whereas the Ag crystals have a diameter of 10-100 μm. This means that Ag atoms are supplied to the crystal only via the steps, and not via diffusion across the top of the crystal. In this way, the Ag atoms are forced to move "down" the steps, where they are then able to diffuse across the wetting layer and nucleate new layers of Ag.

The overall process is very complex even though no silicide formation is observed. 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 obstruct dewetting.

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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. All shaped catalysts are comparable 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 result 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. Tetrahedral nanoparticles are found to be one of the shapes of the nanoparticles during the Suzuki reaction will be discussed.

1:45 PM US5.3
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 reactions such as olefin epoxidation. In this study, initially oxidized TiO2 (110) surfaces were prepared in UHV then defected by controlled exposures to Ar (<200 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 sintered (to larger centered samples with 20 nm) on control samples while sputtered TiO2, nanoparticulate Au is observed with sizes smaller than resolution limit. The density of clusters is correlated to that of the surface defect sites and decrease of cluster size is observed with increased amounts of sputtering. We propose that the 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 at 150 K which is attributed to desorption of propylene from TiO2 sites and the other 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 US5.4
Size-Dependent Changes of the Local Structure in Dodecanethiol-Stabilized Gold Nanoparticles. Anatoly Frenkel1, Talia Harris2, Sarah Nemzer1, Ilana Pister1, Louisette Soussan1, Christopher John Kiely3, Roger Ristau4, Martin Harmer1, Irshad Hussain2, Mostafa A. El-Sayed; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, 1Materials Science and Engineering, State University of New York, Stony Brook, New York, 2Physics and Astronomy, Vanderbilt University, Nashville, Tennessee, 3Metals and Ceramics Division, Oak Ridge National Laboratories, Oak Ridge, Tennessee.

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 nanoparticles 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 nanoparticle 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 the coverage and sulfur adsorption mechanisms in the particles made by these two routes.

2:15 PM US5.5

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 x 50 nm square array of little more than 100 nm diameter optical resonant nanoholes in the sample plane (at a rate of 1.5 nm/hr) over a 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 shifts are 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 US5.6
Enhanced Mutual Solubility in Cu-Ag Alloy Nanoparticles Synthesized by Inert Gas Condensation. S. Imrat Shah1 and Abdullah Ceylan2; 1Materials Science and Physics, University of Delaware, Newark, Delaware, 2Materials Science and Engineering, 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 inert gas at the sample temperature. Two different synthesis conditions were used, one of which had the sample 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 the particles were phase separated. According to the particle size values obtained by Scherrer'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 0% 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 self-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 US5.8
Fundamental Sintering Studies of Metal Nanoparticle Arrays. Christopher John Kiely1, Roger Ristau4, Martin Harmer1, Irshad Hussain2, and Mathias Brust3; 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-dependent properties, there has been great interest in using these particles as building blocks to form "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 supercrysals. The solid state sintering of such self-assembled nanoparticle arrays at first sight seems counterintuitive, however, there are definite benefits to being able to controllably sinter self-assembled nanoparticle arrays into larger entities. For example, in the sintering of micro-scale metal and ceramic particles, it 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 is size-dependent and nanowires form. We have ongoing experimental and theoretical research being carried out in 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 micro-scale particles, form the cornerstone of our analytical approach to this problem. This research is supported by NSF under grant DMR-0306168, and the Pennsylvania Department of Community and Economic Development under contract 26-506-0000.

3:45 PM U5.7

Stability and structural transition of gold nanowires under surface stresses. Jiankuai Diao, Ken Gall, Martin Dunn and Michael I. Hafeli, Department of Mechanical Engineering, University of Colorado, Boulder, Colorado; Nanostructure 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 are very 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 <110> 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 <110> nanowire into an fcc <110> nanowire for relatively large wires. In embedded atom method (EAM) and surface embedded atom method (SEAM) simulations, surface stresses induce yielding and reorientation from an fcc <110> nanowire into an fcc <110> nanowire below critical sizes. The different instability mechanisms and the final structures are 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 PEE M of the Growth and Decay of Dy$\text{Si}_2$ Nanowires. Srinivasan Sundararaya, Manish C. Zeman, W. C. Yang, Lena Fitting and R. J. Nemani, Physics, North Carolina State University, Raleigh, North Carolina.

Nanowires of Dy$\text{Si}_2$ 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. This technique combined with scanning Auger (SAM) and AFM measurements were used to analyze the wire growth dynamics, their ordering, shape and size. We report on the decay of nanowires and their dependences on their initial width. Upon annealing, the growth rate of thin wires (width 20-300 nm) remains constant while the length decreases with time. Meanwhile wider nanowires (width 200-300 nm) tend to break into segments with annealing. Furthermore, some wires are found to be thermally stable up to 1100 °C. We modeled these effects in terms of the epitaxial structure and surface and interface energetics.

4:15 PM U5.9

Growth of Nanowires of β-Na$_3$V$_2$O$_7$ by Metalorganic Chemical Vapor Deposition from Vanadyl Acetylacetonate. M. B. Sahara and S.A. Shiva Shankar, Indian Institute of Science, Bangalore, Karnataka, India.

β-Na$_3$V$_2$O$_7$ is a low-dimensional material with interesting electrical and magnetic behavior, which critically depends on the value of x. β-Na$_3$V$_2$O$_7$ exhibits three phase transitions as a function of temperature: a sodium-ordering transition at $225 \, K$ accompanied by a doubling of the unit cell along b-axis, a transition at $136 \, K$ involving a tripling of the unit cell and a paramagnetic–antiferromagnetic transition at $240 \, K$ accompanied by a tripling of the unit cell. In this work, we report on the growth on glass substrates of nanowires of β-Na$_3$V$_2$O$_7$, measuring 20-200 nm in diameter and 10-30 nm in length, by metalorganic chemical vapor deposition using the β-diketionate complex, vanadyl acetylacetonate, as precursors. Furthermore we use the combination of either templates or catalysts, to exploit the crystal structure anisotropy. Such growth takes advantage of the tendency for surface energy minimization, which promotes oriented growth on smooth nanowire templates. In this work, we show the existence of the bct phase is confirmed by a doubling of the unit cell along b-axis 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 Baderford backscattering spectrometry (BS) studies of vanadium oxide films deposited at different temperatures elucidate the factors leading to the formation of nanowires of β-Na$_3$V$_2$O$_7$. SIMS analysis shows the presence of higher percentage of sodium at the surface than at the interface of the film and the substrate. This is inferred that the formation of nanowires of β-Na$_3$V$_2$O$_7$ is due to chemical vapor transport, i.e., following the formation of β-Na$_3$V$_2$O$_7$ they are due to the reaction of the precursor with the substrate. Films consisting of nanowires of β-Na$_3$V$_2$O$_7$ are not stable up to 1100 °C whereas those deposited at 540°C comprise a mixture of nanowires (β-Na$_3$V$_2$O$_7$) and plates. This is due to the different thermal expansion rates in Ni silicide and the substrate. It is thus inferred that the formation of nanowires of β-Na$_3$V$_2$O$_7$ is due to chemical vapor transport, i.e., following the formation of β-Na$_3$V$_2$O$_7$ 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


Nickel monosilicide (NiSi) nanowires (NWs) were fabricated by the Metal Induced Growth (MIG) method and show the morphological changes due to different growth conditions. A n-type Si (100) wafer was coated with Plasma Enhanced Chemical Vapor Deposition (PECVD) to form a 200-300 nm SiO$_2$ layer as a buffer against Ni diffusion into the Si substrate. Then, Ni was thermally deposited at a thickness of 20-150 nm to serve as a catalyst. This Ni Si ensemble was loaded in a DC magnetic 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 Si ensemble 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 μm and surface coverage of 35/10$^{-2}$ m$^{-2}$. Photoluminescence (PL) data indicate an energy gap of 1.7 eV from a wavelength independent peak at 200 eV. 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, small Si consumption and low formation temperature which allows the use the NiSi NWs as interconnection materials in nanoscale electronics.

4:45 PM U5.11

Surface Diffusion Barriers and Nanostructures Design. Jing Wang, Hanchen Huang and Timothy S. Cale, Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; Department 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).
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.

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$_2$Sn$_5$, 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

Nanocrystalline hard films have attracted increasing interest in modern development of hard thin films. While 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 nucleation of TiN and TiB$_2$ 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 TiB$_2$ 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 nanocrystalline hard films can be tailored to their nanocrystalline state, 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

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 trajectories 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

One of the limitations of nanocrystalline materials 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$_{80}$Fe$_{20}$ and Ni$_{70}$Fe$_{30}$ alloys were produced by the electrodeposition technique and their thermal stability was evaluated as functions of temperature and time. The structure of the samples 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 twin component 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 preeminent, while at high temperatures both lattice and interfacial 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

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 hot and cold rolling 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 nanostructured 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 Mikhiel Hattar, Jong H. Han, Jennifer Ann Gregg, Taher A. Saif and Ian M. Robertson. Materials Science and 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 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.
Morphological Evolution and Stabilization of Nanoporous Gold and Nanoporous Gold, Yi Dong, Anas Mathur, Young-Ju Kim and Jonash Erlsbacher, 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 ultrathin skin of platinum.


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 structure (the (3 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. (3-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 technique. Phase transformation from (3 to bcc 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. These results indicate a significant amount of 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.

The Structure and Stability of β-Ta: A Experimental and Theoretical Study, Aiqin Jiang1, Trevor A. Tyson1 and Lisa Axx1; 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 found 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.

Molecular Dynamics Study of the Prevention of Grain Growth in Nanocrystalline Materials by Use of Doping, Paul Christopher Millett1, R. Pannee Selvam1 and Anshok Saxena1; 1Civil Engineering, University of Arkansas, Fayetteville, Arkansas; 2In Chemical 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 the corresponding 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 Gibbs'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 affects, 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.
laying in multilayers is of major technological importance. Basically, the thermodynamic driving force in multilayers to destroy the layering includes elastic strain and 

allyed to interfacial mixing. Thus, decreases in layer thickness can have a catastrophic effect on thin film stability. An added effect in many systems is the geometrically having a columnar grain structure. A primary question posed is whether multilayer thin films are expected to become 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. 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 nanoscale multilayer thin films by shifting the critical 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 Miller1,2, Nancy Yang1, Cari Herrmann1, Hans Mauer1, George Conrad Stoldt1 and Ken Gall2, 1Mechanical Engineering, University of Colorado, Boulder, Colorado; 2Analytical Materials Science Group, Sandia National Laboratories, Livermore, California; 3Chemistry & Biochemistry, University of Colorado, Boulder, Colorado; 4Lehrstuhl für WerkstoffBünde, 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 diuers 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 de-aged 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 experiments on samples in the curvature 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 layered 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 boundaries, grain cores and a metallographic 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 the 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 nanolaminate alumina coatings by 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 aluminum nitride are used, the film will not exhibit the growth 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. Ongoing mechanisms will be discussed in greater detail in the full paper and presentation.
Plasma-enhanced chemical vapor deposited (PECVD) silicon-based oxides (SiOx) have been widely used in both microelectronics and MEMS (MicroElectroMechanical Systems) to form electrical and/or mechanical components. During fabrication of such microelectronic and MEMS devices, PECVD SiOx 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 SiOx 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 SiOx during deposition and subsequent thermal cycling. A series of in-situ wafer-curve based stress measurements experiments of up to 500°C were conducted for PECVD SiOx films of various thicknesses ranging from below 10 microns to 100 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 few cycles. During subsequent cycling, 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 SiOx film below 500°C, density change plays an important role. However, for the 100 microns thick films at peak temperature, plastic flow 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 SiOx films, including stress hysteresis generation and reduction, and coefficient of thermal expansion (CTE) changes.
these results for CMOS device applications will be discussed. The role of silicide faceting on nucleation and growth kinetics will also be considered.

U8.9  
**Shape and Stability of TiO₂ Nanoparticles in Water: Why the Wulff Construction Is Not Enough.** Amanda S. Barnard,1,2 Peter Zapol1,2,3 and Larry A. Curtiss2,3. 1Center for NanoScales 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 and shape morphology of the deposits. 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 nanotubes to rutile phase transformations. The work has now extended to a new range of 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 indicate 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.

U8.10  
**Environmental Effects on the Structure and Properties of Yttria-Stabilized Zirconia Thin Films.** Jeffrey Robert Pisicka1, Christopher A. Bower2, Brian R. Stoner1,2 and Jeffrey Y. Thompson2,3. 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 work 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 (220–300°C), pressure (5–25 mTorr), and background oxygen levels (0–6% oxygen). Initial studies characterized a select set of properties in relation to deposition parameters including: refractive index, density, and porosity. Structural information has been obtained by X-ray Diffraction (XRD) 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 is strongly dependent on deposition conditions ranging 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 at room temperature. This environmental cycling allowed compressive stresses to be related to water vapor adsorption/abosorption and evaporation. These effects were then evaluated for films, constructed under different deposition parameters, of varying density and porosity. Several models were 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.

U8.11  
**Improving the Adhesion Properties of Nanocrystalline Diamond Films by Bias-Enhanced Nuclear Ion Implantation.** Scott Wölter2, Frabace Paijz3, and Gerardo Morell2. 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 precludes from taking advantage of the many extreme properties of diamond that make it suitable for protective and tribological coatings (i.e. extremely hardness, radiation hardness, chemical inertness). We have employed bias-enhanced nucleation (BEN) physical vapor deposition (PVD) and microwave-plasma chemical vapor deposition (MWCVD) system to implant seed nanostructures in the substrate that favor the formation of a strongly adherent layer at the substrate-film interface. Nanocrystalline diamond films are deposited on the BEN substrates using a hot-film 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 nucleation. Thermal shocks demonstrated the ability of the 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. Ouzouz, 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).

U8.12  
**Thin Films Stress Aging Study using Micromachined Cantilevers.** Christopher Malheira1, Alexandre Andrei1, Sebastiano Brida2 and Daniel Barber1. 1LPM, INSA, Villeurbanne, France; 2Aerospace Division, Estecine 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 performed at room temperature after thermal aging at 150°C. An improved method for measuring stresses using bulk micromachined Si cantilevers with different lengths was 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, 1120°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 topside by DRIE (20 μm depth using a resist as masking). 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 Contrast THIN-550). The definition 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 -260 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 aging of 30 minutes at 720°C in a dry-air 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 3% stress decrease has been pointed out for AlTi after 2 weeks at 150°C / air. 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.

U8.13  
**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
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 topographical (i.e., orientation) 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 in the grains nearly equaxed at high strains. *Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under Contract W-31-109-Eng-28.

**References**


**1 Department of Ceramic and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal; 2Institute of Solid State Physics, Chernogolovka, Moscow distr., Russian Federation.**

Ar$_3$Ni$_{1-x}$ film alloys on Cu substrates with nanoscale grains have been elaborated. The films were deposited by electrical resistive deposition in organic solvents. Only films with a thin oxide (x = 0.5) are obtained by 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 nanocrystalline grains of the alloy (<10nm), that compounded with electron microscopy researches. The size of grains of the alloy depending on concentration (with 3.0-3.5nm for alloys near Ag$_{0.3}$Ni$_{0.7}$, 10nm for Ag$_{0.5}$Ni$_{0.5}$) is investigated. 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 nanocrystalline repeatedly moves up to 600°C. The annealing under stable temperature did not change X-ray spectra. The effect can be explained as a recrystallization in this film and stability of alloy grains with temperature depend from size grains. 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. Brand, Scripta Materialia 44, 2291 (2001) [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)
US10 Residual stress and microstructural evolution in thin film materials for a microfabricated solid oxide fuel cell (SOFC).

David Quinn 1,2, Mark Spearing 2 and Brian Wardle 2; 1 Mechanical 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 sputter deposited SOFC 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.

US20 Structure and Stability of Nano-multi-layer of Metals and Oxides, Somesh Ohnuki 1, Tomohiko Ohkoshi 1, Yuko Kakuta 1, Takanori Suda 1, Seiichi Watanabe 1 and Masahiko Ishino 2; 1 Materials Engineering, Hokkaido University, Sapporo, Japan; 2Ransui Res., Japanese Atomic Energy Research Institute, Kitaz, Tokyo, 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 material. <c-references>


Nanocrystalline self-supported films of functional ceramic materials, for instance, ferroelectrics or ionic conductors, are very promising components for a large variety of micro-electronic 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 intergran 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 intergran 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, intergran strain and stress-induced reorientation of ferroelectric grains are stronger enough to cause rapid (10-20 sec) changes.
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.

US82 Nano-Structured Ultra-Hard Al-Si Films Synthesized by High Rate Codeposition: Velimir Radmilovic 1, David Milin 1 and Ulrich Duhmen 1; 1 LBNL-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 nanostructured Al-Si films on Si substrates. Observations of 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 stress measurements. The stress evolution 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 nano SOFC devices.


Approaches to measuring and then minimizing the strain in electrochemically deposition CdSe nanocrystal films are investigated. Under some conditions, cracking and delamination are seen for films thicker than a critical thickness (~0.8 micron for 3.2 nm nanocrystals), as seen by SEM and AFM, and have 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 electrochemical 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-hexanediol and 1,7-heptanediol. This was supported primarily by the MRSEC Pivotal Grant of the National Science Foundation under Award No. DMR-0215374 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 Boute1, Judith de Goede1, Yves Letertre2, Leonard Medico3 and Jan-Anders Mansson4; 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), flexible substrates 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 organic layers, linear 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 device. Most present studies are used to study the failure behavior 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 nm width) is determined as a function of the thickness of the tensile loaded thin brittle layer, the crack propagation strain can be considered. The wide failure strain of the tensile loaded thin brittle layer in a two-point bending test is significantly larger than the layer thickness. The stress intensity factor is equal to fracture toughness and remain stationary if under compression. The growth paths follow a 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.

Cracks usually nucleate and propagate in microelectronic devices after hundreds or thousands of thermal cyclic loading. The origin of high stress and crack behavior of 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 brittle thin film. The linear elastic strain energy of the thin film 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 brittle layers 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 with the nonlinear model under constant strain amplitude and the crack growth and two ambiguous tasks. In this paper, XFEM (extended finite element method), first invented by Moës et al (UNME, 46:181(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 multiplayer 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 a gradient of the film thickness and the elastic mismatch between substrate and layer. For a high modulus layer on a polymer substrate this stable thickness is significantly larger than the layer thickness. 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.

9:04 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 stresses exceeds the interfacial toughness, fracture normally occurs. Telephone cord delamination 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 produce 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, 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 Dye1, Jo Lo1, Sidney Yip2 and Zhiqiang Suo2. 1Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; 2Citation Materials Science and Engineering, Ohio State University, Columbus, Ohio; 3Division of Materials Science and 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. We find that bond ruptures in Cu and strain at the crack tip remain in 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.
fracture toughness studies on MEMS-scale specimens were conducted. Films will be discussed. Spontaneous dislocation nucleation, we find a higher activation energy with atomically sharp 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 crack 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 using a MEMS scale mechanical testing machine. The experiment was performed in the vicinity of atomically sharp cracks using the Atomic Force Microscopy/ Digital Image Correlation (AFM/DIC) method, 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 m^1/2, 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 m^1/2, microcrystalline diamond 4.9 MPa m^1/2, and ultrananocrystalline diamond 4.6 MPa m^1/2. 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 on the crack tips were computed and used in the calculation of the Mode-II fracture toughness for ta-C.

Composition Effects on Mechanical Properties and Fracture Behavior of Low-k Organosilicate Glass (OSG) Thin Films. Yusoo Lim, 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 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 Backscatter Electron Microscopy (RBS), Wavelength Dispersive X-ray Spectroscopy (WDX), 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.

High-Cycle Fatigue in Freestanding Thin Film Metal Test. Structures, Maarten P. de Boer; Al. David. Corwin; Ghatu Subash; and Michael J. Shaw; Reliability Physics, Sandia National Labs, Albuquerque, New Mexico.

The elastic, plastic and interfacial properties of freestanding metal thin films are of interest for MEMS applications such as radio-frequency devices, microelectrets 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 testing machine we have used fixed a 0.7 micron thick film to a 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 stroscopically 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 a frequency, allowing 10 million cycles to be accumulatable. 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 364 MPa stress assuming Young's Modulus of 300 GPa. We apply 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 fatigue films displayed no obvious damage by SEM, indicating that the fatigue is in the subcritical regime. More detailed SEM analysis and the results of creep experiments will be reported.


Ultra high-cycle fatigue in pure Al thin films. Christoph Eberl1, Ralph Spolenak1, Oliver Kraft2, Franz Kubat3, Werner Ruile4 and Eduard Arzt4,5; 1Max-Planck-Institut fuer Metallkunde, Stuttgart, Germany; 2Forschungszentrum Karslruhe, Karslruhe, Germany; 3Technische Universitaet Clausthal, Clausthal, Germany; 4EPCOS AG, Muenchenn, Germany; 5Institut fuer Metallkunde der Universitaet Stuttgart, 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 an additional applied stress of 4.1±0.3 MPa x 10^{14} cycles could be measured. Instabilities due to 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 indicates 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 cycle density. The development of defect density versus stress 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 thin metal films.
deviations that range from wafer bow to surface roughness, the thin film properties and the process parameters used to achieve the bonds. Hilbert, and has been a long-standing problem 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 bonding. Key conclusions from the model and experiments are that stress relaxation 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, 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 nano grained metal films on silicon substrate, and co-fabricating 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 uniqueness 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 heater 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 a hold temperature. We find that of 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 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 range of 75-110°C. Its relaxed modulus is close to 66% of the unrelaxed modulus, and the activation energy is found to be 1.2 eV 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 measured using a piezoelectric transducer and can be stabilized He 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 low 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 with 5 to 10% of the time 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 one having a different one). The resonance is therefore broadened inhomogeneously. Nonuniform stresses have been directly measured (at a fixed temperature) using x-ray microbeam.2) We suggest that the inhomogeneous stresses revealed in resonance arise from microstructural details (as in the micromachined studies) that result in build up and release of stress at particular sites as the average stress is changing thermally. 1) Seungmin Hyun et al. App.Phys.Lett. 83 7011 (2003) 2) R. Spodden et al. Phys.Rev.Lett. 90 096102 (2003)

2:15 PM • U10.3
Anelastic Behavior of Thin FCC Metal Films. Seungmin Hyun1, Topai Hooghan2, Walter L. Brown2 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 2um and 100nm thickness were prepared by e-beam evaporation or by sputtering onto a silicon nitride membrane substrate. The membrane was strained 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 resonant frequency of a particular membrane the modulus of the Al films is similar to the modulus of bulk Al. The modulus decreases at lower strain rates, indicating anelastic behavior. Recovery occurs in two stages. The stress relaxation behavior is 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. 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 Cervello1, Peter M. Derlet2, Dan Grutter1, Helen Van Swygenhoven1 and J. Hooghan2; 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 in situ x-ray data and exploiting the 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 thing polycrystalline Si are presented.
factor, find that relaxation never proceeds as far as predicted by models for supersaturation during growth. During growth, the dislocation density stress intensity factor resulted in repeatable incremental crack silicon is attributed to its crystalline structure and the associated created in the micro-tension specimens using a micro-indenter. Direct displacement fields were found to be in excellent agreement with cleavage anisotropy. Crack propagation is controlled by grain density does not rise significantly until a thickness well beyond the incremental crack growth in brittle polycrystalline stress measurements have been taken during MBE growth of In$_2$Ga$_{1-x}$As/GaAs and In$_x$Al$_{1-x}$As/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 behavior 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 rate showed that the 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 increase 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. Che, K. Jonnalagadda and I. Chasiotis

Materials Science and Engineering, University of Virginia, Charlottesville, Virginia;

Mechanical 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 micron thick and 50-90 micron wide gauge sections were fabricated using the MUMPs process. Atomically sharp edge cracks with lengths that varied between 6-23 microns were created by a combination of micro-indentation measurements of Mode I crack tip displacement fields with nanometer resolution were conducted using atomic force microscopy (AFM)/Digital Image Correlation (DIC) method. The specimens used in the AFM/DIC micro-machined 2 micron 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 ± 0.07 MPa*sqrt(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 measured using microscopically stress intensity factor $S_{Ic} = 0.84$ MPa*sqrt(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 as well. Finally, the crack grew catastrophically at stress intensity factor, $K_{IC} = 1.06$ MPa*sqrt(m), which was very close to the average fracture toughness recorded for polycrystalline crack silicon. Further validation for these observations was provided by the corresponding micro-cracks observed in adjacent grains. The 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 presence 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.
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.
Tanass D. L., Zh stray Huang, Zh yang S., Stephanie P. Lacour.
Department of Mechanical Engineering, University of Illinois at Urbana-Champaign.

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
observations show that:

1. Film thicknesses show an increase in effective modulus with increasing
thickness.
2. The 0.50 mm film has similar but smaller grain sizes and higher effective
modulus.
3. The 0.25 mm Al film was observed to have a higher effective modulus than
the 0.50 mm Al film.

These experiments are promising for applications in biological systems and severe dynamic environments.

U11.2
Microstructure evolution across interfaces of heterogeneous
metal systems under ultrasonic impact. Yu unhong Li,
Yinon Ashkenazy2 and Robert S. Averbach.
Computational Science and Engineering, University of Illinois at Urbana-Champaign.

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
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 Helaen Van
Sweyghenhoven; ASQ/NUM, Paul Scherrer Institute, PSI-Villigen,
Switzerland.

The high frequency phonon properties of a computer-generated
nanocrystalline (nc) Fe: Ni are investigated by directly calculating the
on-site phonon Greens function using a recursion technique based on a
continued fraction representation.

It is found that the high frequency
vibrational modes and atomic activity with in 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
Pugetrotet and George Martin; CEA-Saclay, SBMP, Gif sur Yvette,
France.

Thick Ag films deposited onto polyimide Ni substrates, dewet the
substrate when annealed at high temperatures in an 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 equaxed 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 in-plane 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, Interface Sci. 11, 379 (2003).

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 templating growth of nanostructures 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, sharp one at the oxide-Ni interface with a small amount of Cu present throughout the nanosecond timescales corresponding to elemental systems Ni, Au, Cu, and Cr, along with a discussion of electrochemical deposition of thin films will be presented. The in situ observations are correlated to the presence of the thin Cu layer. These observations are correlated to the in-plane 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, Interface Sci. 11, 379 (2003).

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Today there are significant new materials challenges relating to integration of metallic thin films in advanced device applications. These include the growth of nanostructures 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, sharp one at the oxide-Ni interface with a small amount of Cu present throughout the nanosecond timescales corresponding to elemental systems Ni, Au, Cu, and Cr, along with a discussion of electrochemical deposition of thin films will be presented. The in situ observations are correlated to the presence of the thin Cu layer. These observations are correlated to the in-plane 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, Interface Sci. 11, 379 (2003).

Morphological and Stress Evolution During Thin Film Electrodeposition. Jianhui Liao, 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 was 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 system and the deposition conditions. These behaviors are 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 this films observed associated 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 the previously studied films, the relaxation was governed by 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. [U1.8]


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 tungsten film. The technique is 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 and 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. [U1.9]


Phase separation behavior in thin CoCu-1-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 Ti below Ti = 350 °C, phase separation in CuCo films of all compositions stabilizes at high doses (by 5x1015 ions/cm²), indicating the existence of a metastable state. Below these doses, a disordered and metastable states for these alloys under irradiation. At temperatures higher than 350 °C, nanoscale-like coarsening is observed. At low temperatures (room temperature and below), Fe/CuZr (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 Fe and CuZr 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) 2882). [U1.10]

Molecular-Dynamics Study of Ductile Void Growth Mechanisms in Metallic Thin Films. M. Rauf Gungor and Dimitrios Mamoudas; 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. Towards these goals, atomic-scale modeling based on molecular-dynamics (MD) simulation provides 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 approach is based on in-situ 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. Our MD simulations provide a detailed view of how void growth is initiated at the void surface and subsequent dislocation propagation; as a result, a plastic zone forms around the void. Our simulations show that void 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, Tokuki Himuro, Yushio 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 grating 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, the larger the scattering angle needed to get the X-ray depth profile 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 film thickness. 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 at a temperature below the 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, 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 MEMS Interconnects, Alberto Cucinotta,1 Mansel Koslosky,2 Michael Ortiz,2 Daniel Pantuso4 and Sadasivan Shankar1,2, Dept. of Mech. and Aerosp. Eng., Rutgers University, Piscataway, New Jersey; 2Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico; 3Galact, Caltech, Pasadena, California; 4Intel Corp., Hillsboro, Oregon.

Due to increasing demand in electrical performance, new materials are developed and integrated for future generations of interconnects. A major source of uncertainty about structural integrity and possible failure mechanisms becomes a key concern during the circuit interconnect process development phase. Hence, having predictive and accurate theoretical micromechanical models is 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 competition of different physical mechanisms and are not well understood. This 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 the void growth and stress relaxation driven by such and their interaction 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 basic grain sizes, 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 void nucleation and propagation of threading dislocation loops. 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.

U11.13  **In-situ TEM Study of Dislocation Mechanisms in Nanoscale Cu Interconnects.** Jin Ho Ah and Paulo Forreiro; 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 density and shrinking the device size. In order to achieve this goal, it is crucial to continue decreasing Cu interconnect widths. However, as downsizing 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 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. The microstructure of 1.8 micron 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 downsizing of these interconnects continues.

U11.14  **Electroless Gold Nanoparticle Film Deposition on III-V Semiconductor Surfaces.** Hyunseul Lim1, Byung-Oh Choi1, Kwang Young Kim1, Carlos Carraro2 and Roy Maboudian2, 1Dept. of Advanced Industrial Technology, Korea Institute of Machinery and Material, Daejon, 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 solutions of AuCl₄⁻. Deposition process proceeds via galvanic displacement in the absence of acid, pH adjusters, external reducing agents. The controlled depositions of nanoparticles are performed by modulation of the plating parameters such as concentration, temperature, and immersion time. The deposition reaction is first order with respect to the plating parameter and zero order with respect to the substrate surface but not to pH. In this manner of deposition can be expected to yield 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.
Repeated laser pulse melting of copper/silver multilayers and co-deposited copolymer films were 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. A strong dependence in the film thickness on the silver 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 being 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 where systematically investigated with cross-sectional and plane view TEM, and STEM, in addition to RBS and XRD. Experimental results are compared with computer simulations.

Effect of Nanoscopic Fillers on the Viscoelastic Response of Polymer Systems. Jean Harry Xavier1, Miriam Rafaelovich1, Jonathan Sokolov1, Young-Soo Seo2 and Abraham Ulman2.1. Materials Science, Stony Brook University, Stony Brook, New York; 2 Chemical 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 (Tg) was depressed by 10°C 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 was increased significantly for the Au 10 nm, and constant for the Au 3 nm and cloisite 6 clay. Values for zero shear 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.


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 imperfections, which can be up to 10% below 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 probe these competing processes, we have performed 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 competition of polymer microdomain coarsening, which 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 angles, 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 film 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. Huhm, S. J. Sibener, J. Chem. Phys. 114, 4730 (2001); [2] S. Sundrani, S. J. Sibener, Science 304, 273 (2004); [3] S. Sundrani, S. B. Darling, S. J. Sibener, Langmuir 20, 5091 (2004); [4] P. Lambrou, T. P. Russell, G. J. Kellogg, A. M. Hayes, P. D. Gallagher, S. K. Satija, Phys. Rev. Lett. 72, 2890 (1994).

Stress Evolution in PMMA Spin Films. Agita M. Bowles and Frans Spaepen; Department 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.


Styrenic block copolymers are among the most widely used polymeric materials today. Their applications span a wide range of industries, from automotive, footwear, 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.


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), aluminum alloy, and silicon substrate, which was regarded as the main cause for the large Tm depression. The entropy effect was regarded as the main cause for the large Tm depression. The interfacial energy and the branching concentration play an important role in the melting entropy of the ultra-thin films, so the large Tm depression was attributed to an increased melting entropy.
Another consequence from shear in the film when the shear rate due to dewetting is larger film thickness. We attribute this to the pinning of the polymer chains substrate. Samples prepared in this manner had lower viscosity than spun cast a PS layer that was smaller than the radius of gyration. The Thermodynamics of Polymer Thin Films. Sanat Kumar, RPI, Elec. Eng. and Comp Sci., University of Michigan, Ann Arbor, Michigan. This behavior confirmed the "two-fluid theory". Another consequence of the surface interactions are large regions beneath the probe layer confined along multiple dimensions, and the surface to volume ratio is 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 probe layer's surface. 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 the 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". A finite element simulation of the surface interactions are large regions beneath the probe layer confined along multiple dimensions, and the surface to volume ratio is 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 probe layer's surface. 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 the 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".
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 energetic 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 strips 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 metalization 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.