SYMPOSIUM O

Mechanisms of Surface and Microstructure Evolution in Deposited Films and Film Structures

April 17 – 20, 2001

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*Invited paper
Based on a temperature dependent, quantitative STM analysis for homoslitipal growth and erosion of Pt(111) several atomic scale mechanisms and phenomena responsible for coarsening of monolayer pits are discussed: (i) noise assisted coarsening, (ii) coalescence coarsening, (iii) step edge diffusion present only during deposition or erosion, (iv) step edge diffusion present even in the absence of deposition or erosion resulting from thermal creation of species being mobile along steps and (v) step atom detachment. For Pt(111) mechanism (iv) - the thermal creation of species being mobile along the steps - is found to be decisive. Only when step atoms are thermally excited as kinks coarsening takes pace. It is argued that for many low index surfaces this coarsening mechanism is likely to be operative. Instead of a surface diffusion current driven by changes in surface curvature frequency, induced by a nonequilibrium tension. The origin of coarsening, it appears that even at high temperatures coarsening may be driven only by differences in curvature along contours of constant height.

9:00 AM 9.1.2 HAVE WE FOUND THE FINAL EXPLANATION FOR THE ONSET OF RAPID INTERLAYER MASS TRANSPORT? Margret Giesen, Harald Bach, Forschungszentrum Jülich, IGV, Jülich, GERMANY.

In previous STM investigations of multilayer Cu island decay on Cu(111) we reported on the observation of a novel rapid interlayer mass transport mechanism [1, 2]. The rapid island decay sets in when island edges in a multilayer island stack approach below a critical distance. For Cu(111), this distance was found to be about 6.5 A. The atomic rows independent on temperature. We could also show that the island decay rate could be explained if one assumes that the step edge barrier for interlayer mass transport vanishes if the island edges are closer than 6.5 A. As a result for the vanishing of the step edge barrier we proposed an electronic effect. Assuming that island edges served as impenetrable barrier for electrons we could show that in the case of Cu(111) the surface state would be shifted beyond the Fermi level due to quantum confinement at the critical distance. Rapid island decay is also observed for Ag(111). Here one would expect the critical island edge distance to be about 24 A.

9:15 AM 9.1.3 RAPID ALOXID ISLAND DECAY ON Cu(111): A KINETIC MONTE CARLO SIMULATION STUDY. Mats I. Larsson, Karlstad University, Karlstad, SWEDEN.

Kinetic Monte Carlo (KMC) simulations are used to investigate the recent scanning tunneling microscopy (STM) measurements of fast decaying zumion islands on Cu(111) performed by Giesen, Schulte, Ikoning and Bach [1]. The KMC model is a full diffusion bond-breaking model including nearest neighbor as well as second-nearest neighbor interactions. The modeled potential energy barriers are found to correspond well to the experimental ones for the studied temperature range 314 K to 500 K. The investigation consists of two parts. Firstly, reduced activation energies for adatom migration along close-packed step edges are shown to be very important to obtain rapid decay of the islands, in accord with the STM measurements. To obtain the best correspondence to the measurements, the 1D Ehlich-Schwoebel (ES) barrier for adatom hopping around island corners has to be fully suppressed. Secondly, for encounters between steps in adjacent atomic layers of an island it is demonstrated that a moderately reduced activation energy for interlayer adatom transport is enough to obtain good correspondence between simulations and experiments, provided that the 1D ES barrier for corner transitions is reduced to zero. The results presented in this report are interesting because they demonstrate that the diverse microscopic effects can be generated by very small changes of the potential energy barriers that are controlling the surface diffusion rates. [1] M. Giesen, G. Schulte, Ikoning, and H. Bach, Phys. Rev. Lett. 80, 592 (1998).

9:30 AM 9.1.4 TEMPERATURE-DEPENDENCE OF MOUND FOUNDATION DURING MULTILAYER GROWTH OF Ag(Ag100) FILMS. K.J. Capersen, A.R. Legson, C.R. Stoldt, P.A. Thord, J.W. Evans, Iowa State University, IA.

A current challenge is to characterize the dynamics of mound formation induced by step-edge barriers inhibiting downward transport during multilayer growth of homoslitipal films. Available experimental data has been limited, often estimating roughening and coarsening exponents for only a single temperature, and being subject to over interpretation. Thus, we have performed a comprehensive VSTM study of mound formation in the Ag/Ag(100) system between 175 K and 300 K [1]. Bahrns was interpreted using detailed atomistic modeling which precisely describes irreversible island formation in each layer, and incorporates non-uniform step-edge barriers, a realistic treatment of periphery diffusion at island edges, and downdown funneling deposition dynamics [2]. All these aspects of the realistic atomistic dynamics are important for the description of mound dynamics in the Ag/Ag(100) system, including such features as the strong temperature-dependence of mound coarsening and slope selection. [1] K.R. Stoldt, K.J. Capersen, et al., Phys. Rev. Lett. 85 (2000) 808; [2] K.J. Capersen, C.R. Stoldt, et al., Phys. Rev. B, submitted (September 2000).

9:45 AM 9.1.5 TEMPERATURE DEPENDENCE OF THE ROUGHENING EXPONENT α FOR THE GROWTH OF Cu ON Cu(001). Cristian E. Botir, William C. Elliott, Paul F. Meoli, University of Missouri-Columbia, Department of Physics and Astronomy, Columbia, MO; Peter W. Stephens, State University of New York, Department of Physics, Stony Brook, NY.

X-ray scattering has been used to study the kinetic roughening of Cu(001) surface during homoslitipal growth. The coverage dependence of the root-mean-square (rms) roughness, , obtained from specular reflectivity data, was measured for temperatures between 160 K and 370 K. All temperatures the rms roughness was found to increase as a power law with , for coverages, , ranging from 3 to 96 ML. The roughening exponent, , was observed to depend on temperature of the substrate: at low temperatures (T < 200 K) , while above 300 K, the exponent decreases, reaching 1/3 at T = 370 K. The difference between these results and those of a previous helium-scattering measurement will be discussed. Support is acknowledged from NSF under contracts [PWSDMR-9220528 and (PPM, CEB, WCE) DMR-9220827 and MISCON under DOE grant DE-FG02-89ER45427. The SUNY X3 beam line is supported by the DOE, under contract DE-FG02-89ER45231 and the NSLS is supported by the DOE, Division of Materials Sciences and Division of Chemical Sciences.

10:30 AM 9.1.6 SIMULATING FILM GROWTH WITH ACCELERATED DYNAMICS METHODS. Arthur J. Lichtenberger, University of New Mexico, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM.

A significant problem in the atomistic simulation of film or crystal growth is the time scale limited by the simulation of the atomic dynamics (MD) method. In the simulation of vapor deposited growth of a film, MD is ideally suited for describing the individual deposition events, but, being limited to nanoseconds, is hopelessly inadequate for describing the accumulated diffusion and redeposition events that occur during the milliseconds or seconds before the next atom deposition. To overcome this problem, we have been developing accelerated dynamics methods that retain full atomistic, dynamical detail in describing grain-to-grain diffusion events, but which reach much longer time scales than MD. In essence, these methods (hyperdynamics, parallel-replica dynamics and temperature accelerated dynamics) achieve this extension in time scale by sacrificing information about the vibrational dynamics. In particular, we have recently found that the temperature accelerated dynamics method is ideally suited for studying crystal growth at low temperatures (e.g., roughly 100 K) below which the computational load can be in the billions. We have been performing metal grain growth simulations at deposition rates in the monolayer/second range, enabling direct comparison with recent surface-science experiments. I will discuss how this is achieved and present our latest results.

11:00 AM 9.1.7 AN ACCELERATED KINETIC MONTE CARLO METHOD FOR SIMULATION OF THIN FILM DEPOSITION. David G. Eastham, Division of Engineering and Applied Science, California Institute of Technology, CA; Robert V. Kohn, Courant Institute of Mathematical Sciences, New York University, New York, NY.

Kinetic Monte Carlo (KMC) simulations of epitaxial thin film growth can be slow, since the timestep is limited by the fastest events, which
are typically the nearest-neighbor migrants of adatoms on terraces. We present here an accelerated scheme in which adatoms are programmed to migrate over long distances without returning to the terrace, up to the distance to the nearest step. Precomputed solutions of a steady-state diffusion equation in a simple geometry are used to generate the necessary propagation event probabilities. All other events are treated by KMC. In simplest form, the algorithm is valid only in the low adatom density limit, in which each adatom executes an independent random walk until it reaches a step or desorbs. However, by constraining the maximum independent propagation distance, a migration may be extended to higher adatom density and even used in the presence of island nucleation. This algorithm is substantially faster than standard KMC when the diffusion length is large. Preliminary numerical comparisons have shown decreases in total simulation time in some cases of more than an order of magnitude.

11:15 AM  O1.8
AN INTEGRATED MOLECULAR DYNAMICS AND MONTE CARLO APPROACH TO STUDY EPITAXIAL DEPOSITION OF SILICON. Sreen Soma Sai, Biman Bhattacharya, Chemical Engineering Department, Washington University, St. Louis, MO; Ronald Lecat, Department of Chemistry, Washington University, St. Louis, MO.

Epitaxy on wafers deposits a thin layer of high-purity silicon to create a layer with a different doping concentration and to rid the surface of device-killing voids or crystal-originated pits. A complete description of this process would require molecular details of the motion on the surface and modeling of the growing of the silicon crystal. However, the extremely different time scales of these processes make it impossible to study them together. Hence, we use an integrated Molecular Dynamics and Monte Carlo approach for this problem. The key steps in the epitaxial growth of high-quality single crystals are the adsorption, diffusion, and desorption of various species on the crystal surface. As chlorosilanes are the commonly used precursors for this deposition, we have investigated the rates and mechanisms of surface diffusion and desorption of silicon, hydrogen and chlorine adatoms on a plane Si (100) surface with single-height steps using molecular dynamics simulations. A detailed finite temperature study of these processes was hitherto not feasible with the existing Molecular Dynamics (MD) techniques due to the long time scales involved. We have circumvented this limitation by developing a classical-density functional inspired MD simulation scheme that allows us to calculate the free energy surfaces of various processes. The rate is determined by using simple transition state theory from the Molecular dynamics determined activation barrier and the pre-exponential. In order to simulate the growth of Si (100) crystal, Monte Carlo scheme was used in which larger system sizes and time steps were used. The rates of the essential steps in the growth were determined by molecular dynamics explained previously and Monte Carlo simulations were performed to track the motion of different adatoms on the Si (100) surface and to elucidate the various steps in epitaxial growth of Si (100).

11:30 AM  O1.9
ADDITIONAL ENHANCED EVOLUTION OF SURFACE NANOSTRUCTURES: COARSENING AND SMOOTHING OF Ag ISLANDS ON Ag(100). Rinat G. Theye-Lawson, Iowa State University, Dept. of Chemistry, Jim Evans, Iowa State University, Dept. of Mathematics, Ames, IA.

We report the effects of oxygen on the nucleation, and subsequent coarsening, of Ag islands on Ag(100). Both of these processes—nucleation and coarsening—are ultimately controlled by atomistic-scale diffusion processes. These processes, with and without background gases, provide indirect evidence regarding their effect on atomistic-scale diffusion processes. These UHV experiments were performed using High-Resolution Low Energy Electron Diffraction and Variable Temperature Scanning Tunneling Microscopy. Submonolayer and multilayer Ag deposition were performed in situ within a UHV chamber. The Ag(100) single crystal was excited by 250K and simultaneously exposed to the gas of choice, while subsequent coarsening was monitored after evaporation of the gas. Spot profile analysis shows the nucleation of islands is unaffected in the presence of oxygen, but the rate of subsequent coarsening is enhanced. STM reveals that the known coarsening mechanism for Ag/Au(100), island diffusion/coalescence, has changed. In the presence of oxygen, Ostwald Ripening becomes active and coexists with island diffusion/coalescence in the evolution of the surface islands.

11:45 AM  O1.10
EFFECT OF SiON THE SURFACE MORPHOLOGY OF CLEAN AND Ag COVERED Ge(100). Lisa H. Chan, and Eric I Altman, Department of Chemical Engineering, Yale University, New Haven, CT.

The interaction of Sb with Ge(100) was investigated as a function of substrate temperature and Sb coverage using temperature-programmed desorption (TPD), low energy electron diffraction (LEED), ion scattering spectroscopy (ISS), and scanning microscopy (STM). An Sb desorption peak at 550 K was observed, while a second desorption peak at 980 K was attributed to Sb bound to the Ge surface. Four basic types of Sb clusters were identified at 320 K. At 520 K, Sb started to desorb. In simple terms, this indicates that the Sb physisorption physical adsorption was observed at 550 K while a second desorption peak at 980 K was attributed to Sb bound to the Ge surface. Interdiffusion between Sb and Ge was found in both the islands and the original surface layer. Interdiffusion, however, was limited between 520 K and 620 K when the Ge surface was covered with 1 ML or more of Sb, resulting in the smoothest Sb-terminated Ge surfaces. Regardless of how the Sb layer was prepared, annealing at 800 K roughened the surface severely and increased the amount of exposed Ge, even though the Sb desorption peak at 980 K decreased. At 980 K, the intermixed Ge layer was attributed to the increased surface area enabling Sb-Ge exchange. The surface roughening was attributed to the increased surface area enabling Sb-Ge exchange, without forming a second layer of Ge beneath the surface. Antimony is used as a surfactant to promote the growth of GaAs films. The results demonstrate, however, that intermixing can lead to the surfactant layer. The second layer of Ge is not necessarily controlled. Subsequent growth of Ag on Sb-terminated Ge(100) surface was studied using LEED and STM.

SESSION 02/R2: JOINT SESSION

EPITAXIAL GROWTH

Chair: Thomas W. Mischke and Arthur F. Voter
Tuesday Afternoon, April 17, 2000
Salon 7 (Marriott)

1:30 PM  O2.1/R2.1
CONNECTIVE STEP-BUNCHING ON CRYSTAL SURFACES. Andrew Zangwill, School of Physics, Georgia Institute of Technology, Atlanta, GA; Naot Imai, Daniel Kandel, and Michael Schatz.

Recent theoretical work predicts that uniform step-flow growth can be unstable to step-bunching during heteropolyhedral crystal growth. In this talk, I show that step-bunching of this kind can occur via a convective instability. The convective nature of the instability implies a mechanism for the surfactant effect that is common in hydrodynamics (and plasma physics) that should allow experimenters to discriminate between strain-induced bunching from other types of bunching. More significantly perhaps, convective bunching lends itself to external control in a manner that suggests a new approach to nanoscale morphological patterning of crystal surfaces.

2:00 PM  O2.2/R2.2
THE DECOMPOSITION OF bBAA ON SILICON FOR COPPER CVD. Cho-Chen Chang, Ing-Jye Huang, National Taiwan University, Department of Chemistry, Taipei, TAIWAN, ROC.

Parallel to the shrinkage of feature sizes to 0.18 μm and below in integrated circuit fabrication, the emergence of a class of chemistries that may be employed as CVD precursors of copper. Among the copper precursors used, β-diketone complexes exhibited a high sublimation rate and a low pyrolysis temperature. The present study evaluates the possibility of using β-diketone complexes as precursors for copper. The β-keto ester appears to alter the properties of the metal β-diketone complex substantially, leading to an improvement in the precursor reactivity. Static secondary ion mass spectrometry studies on the adsorption and decomposition of the L-β-diketone complexes on the β-diketone complex on Si(100) show that, at low doses, all bBAA molecules dissociate readily upon adsorption on the substrate surfaces at substrate temperatures as low as -160°C. The dissociation may occur through bBAA bonding via the ester or the diketo oxygen to the surface. The bond scission occurring at the Cu-CO bond yields isobutene and surface hydroxyl species. In addition, the Cu-COO bond scission induced by bBAA surface bonding mainly via its carbonyl oxygen after oxidative dehydration, whereas the isobutene yields carbon dioxide and isopropenyl species. Upon acquiring surface hydrogen, an endo-keto conversion takes place for isopropenyl species to yield acetone, even at low substrate temperature of less than -120°C. The acetone pathway dominates the cleanup of the Cu-COO bond over the carbonyl oxygen pathway. Possible bBAA decomposition mechanisms at high exposures are also discussed.

2:15 PM  O2.3/R2.3
RATE-EQUATION APPROACH TO ISLAND CAPTURE-ZONES AND SIZE DISTRIBUTIONS IN SUBQUANTUM-LAYER GROWTH. James G. Amar, Univ. of Technology, Beijing, China; Shigeo Aoki, Tokyo, OH; Mitsu N. Pitcescu, Pesquedon Family, Emory Univ., Dept. of Physics, Atlanta, GA.

We present a quantitative rate-equation approach to irreversible
submonolayer growth on a two-dimensional substrate. Our method explicitly takes into account the existence of a denuded ("capture") zone around each grain, the fluctuating capture area, and the correlations between the size of an island and the corresponding average capture zone. The evolution of the capture zone is described by a set of von Karman-type evolution equations which are coupled into rate equations for the island densities through local rates of monomer capture. The combined set of rate equations leads to a fully self-consistent calculation of the size- and coverage-dependent capture numbers. The resulting predictions for the capture zone size and monomer number densities are in excellent agreement with experimental results and Monte Carlo simulations.

The corresponding island-size distributions and their dependence on coverage and deposition rate are also accurately predicted.

2:30 PM 02/4 R2.4

It is demonstrated how the growth mode of thin metallic films on insulating substrates could be theoretically predicted combining thermodynamic approach and ab initio calculations for low-covered ordered metal/insulator interfaces. Theory predicts conditions for monolayer growth via spinoidal decomposition, or for metal cluster nucleation and growth mode. This is illustrated by calculations for a long-defect array of Ag on MgO substrate. Our ab initio calculations predict high mobility of adsorbed Ag atoms on MgO substrate even at low temperatures which stimulates their agglomeration.

2:45 PM 02/5 R2.5
THE EVOLUTION OF SURFACE MORPHOLOGY CAN BE DOMINATED BY BULK (NOT SURFACE) PROCESSES. N.C. Bartelh, J.A. Nolte, and K.F. McCurry, Sandia National Laboratories, Livermore, CA.

The processes that control evolution of surface morphology are almost always found to occur in the topmost layer or two surface layers. However, in the work reported here we show that the smoothing of the NiAl(110) surface is dominated by direct exchange of bulk defects (vacancies) at the surface steps, not by surface diffusion. This conclusion is reached by measuring the kinetics of island decay using low-energy electron microscopy. Remarkably, the decay rates are constant in time and totally independent of the local environment (e.g., the width of the immediately adjacent terrace or the size of nearby islands). Given this lack of evidence for any surface current between islands of different curvature, we deduce that surface diffusion is not important to the smoothing process. Instead, we unambiguously show that bulk vacancies are responsible for the smoothing by directly measuring the rate of vacancy flow between bulk vacancies and the surface when the sample temperature is changed. Surface steps advance when temperature is increased and recede when temperature is decreased. These changes result from the increase (decrease) in bulk vacancy concentration for a temperature increase (decrease). Remarkably, the size change accompanying a temperature change is always precisely proportional to the perimeter (step length) of the island. Thus, we conclude that the atoms at surface steps undergo direct exchange with bulk vacancies. Since the steps are interacting directly with the bulk, the surface dynamics are independent of the local environment (i.e., step density and curvature). This conclusion is contrary to (current) conventional wisdom. By sinusoidally varying temperature and measuring the phase shift of step motion as a function of frequency, we can also estimate bulk vacancy diffusion constants.

This work was performed under the U.S. Department of Energy contract DE-AC04-94AL85000 and supported by the Office of Basic Energy Sciences, Division of Materials Sciences.

3:30 PM 02/6 R2.6
EXPLORING EPITAXY FOR NOVEL MAGNETIC MATERIALS. Ray Clarke, Alejandro Lakshmikumar, Cristian Uher, Vladimir Stoca, Yongguang Zheng, University of Michigan, Ann Arbor, MI.

Ever since lode stones were first used for navigation nearly a thousand years ago, microscopic interactions have played a key role in the development and application of magnetic materials. The ability to control magnetic properties through a material’s microstructure, and now nanostructure, is central to all current magnetism technology from high density magnetic media to the development of super magnets. The advent of epitaxy as a practical method for producing high quality thin film materials has opened up many new possibilities for novel magnetic structures, extending the range of growth control down to the atomic level. This presentation will focus on the use of template epitaxy to achieve well-defined microstructures and nanostructures in magnetic thin films, in many cases leading to micromagnets in bulk polycrystalline form. We illustrate the emerging effects of magneto-crystalline anisotropy, epitaxial strain, and shape anisotropy, drawing on our recent work in the growth of ultrathin cobalt films on Cu-covered Si(100) wafers. An important feature of this work is the interplay between low-temperature deposition and mass transport kinetics influenced by carefully controlled annealing processes.

4:00 PM 02/7 R2.7
VACANCIES AND SURFACE MORPHOLOGY DURING LOW TEMPERATURE HOMOEPITAXY OF METALS. Cristian E. Botez, William C. Elliott, Paul F. Miedl, University of Missouri-Columbia, Department of Physics and Astronomy, Columbia, MO, Peter W. Stephens, State University of New York, Department of Physics, Stony Brook, NY.

X-ray scattering experiments on the homoepitaxial growth of Ag and Cu show that high vacancy concentrations can be achieved during low temperature deposition. A unique aspect of x-ray scattering is its ability to probe the surface structure and the surface morphology simultaneously. It is observed that the vacancies, which can attain concentrations on the order of 2% in Ag, extend throughout the thickness of the deposited film. Moreover, the vacancies are found to faceted on the evolving surface morphology for certain nucleation sites. The effect of vacancies on the surface morphology will be discussed in terms of prior studies of kinetic roughening in these systems.

Support is acknowledged from the NSF under grants (PWS), DMR-9524025 and DMR-9524233, and the US-DOE (DOE) under contract DE-FG02-82ER45227.

4:15 PM 02/8 R2.8
CLOSING THE GAP BETWEEN CRYSTAL-GROWTH EXPERIMENTS AND SIMULATION RESULTS OF TEMPERATURE-ACCELERATED DYNAMICS SIMULATION OF Ag(Ag100). F. Montesanti, S. Swaminathan, M.R. Sorensen, T.C. Germain and A.F. Voter, Los Alamos National Laboratory, Los Alamos, NM.

We investigate the first stages of growth of Ag(Ag100) at low temperature. By using the temperature accelerated dynamics (TAD) method [1] we are able to extend the standard molecular dynamics time scales by ~10 orders of magnitude, so that experimental deposition fluxes are matched. Indeed, we deposit 4 ML of Ag for a total simulation time of ~1 minute. No a priori information on the relevant diffusion mechanisms is needed. We show that activated events can play an important role in determining the growing-surface morphology even at temperatures as low as 40 K. Two different impinging-atom moments are considered: 0.25 eV and 0.025 eV. We show that by lowering the momentum, the role of activated diffusion events becomes crucial and the surface roughness increases (Gaussian roughening) to adatom-vacancy dominated roughening.


4:30 PM 02/9 R2.9

In a continuing effort to probe the role of atomic insertions during hyperthermal ion deposition, thin copper films have been deposited on single crystal copper substrates and characterized using a UHV Scanning Tunneling Microscope (STM). The results of these insertions provide a net downhill current that offsets the roughening effect due to uphill "Schwoebel" currents leading to a net smoothing of the surface. Thin films have been grown at several different energies targeted to observe a crossover from atomic deposition to adatom-vacancy dominated roughening. Copper thin films are deposited near 20 eV using a mass selected ion deposition system that allows precise control over the energy of constituent atoms. Experimental observations are compared with a sophisticated Kinetic Monte Carlo and Molecular Dynamics hybrid (KMC-MD) simulation.

4:45 PM 02/10 R2.10
STUDIES OF SURFACE PATTERN ON Si(100) SURFACE AFTER Cu AND Sn DEPOSITION. Qin Hu, Mart Zobel-Altmann, Ian V. Mitchell, University of Western Ontario, Department of Physics and Astronomy, London, Ontario, CANADA.

We report our studies on Si(100) samples with Cu and Sn deposited in an MBE system followed by annealing. Imaging the surface pattern
with AFM and SEM shows that Cu-Sn non-uniform clusters were formed with their shape not sensitive to the order of metal deposition. Changing the relative amount of Cu and Sn a range of varying morphologies were observed. Pyramidal pits were found on the S(100) surface with Cu-Sn clusters nucleating and growing from those pits. The direction of growth of the pyramidal pits and clusters is <100>. The layer-by-layer growth mechanism of the Cu-Sn clusters differs from that of pure Sn clusters, leading to the discussion of the growth of epitaxial structures.

SESSION 03: POSTER SESSION
Chairs: Jacques G. Amor and M.V. Romann Mruty
Tuesday Evening, April 17, 2001
8:00 P.M. Salom 1-7 (Marriott)

03.1 SIMULATION STUDY OF COPPER CLUSTER DEPOSITION.
Jin Chul Kang, Jeong Woo Kang, Ho Jong Hwang, Semiconductor Process and Device Laboratory, Dept. of Electronic Engineering, Chung-Ang Univ, Seoul, KOREA.

We investigated copper cluster deposition with classical molecular dynamics simulations. We have examined variations of the substrate temperatures, and the number of the disordered atoms during the simulations. We analyzed the properties of copper cluster impacts, such as sticking and sputtering, intermixing, spreading index, surface roughness and film density, as functions of the cluster size, impact angle and initial energy. At the impact angle of the cluster increases, the sputtering ratio increased. In the case of cluster with the same energy per atom, the sputtering ratio and the root mean square (rms) of the surface are proportional to the cluster size. As impact angle increases, the spreading index and intermixing increase. When local area reach melting state on the surface around impact point of an energetic copper cluster during a few ps, intermixing was easily achieved and a good epitaxial film with bulk density was grown.

03.2 MODELLING Cu DIFFUSION INTO Ta BARRIER. Chun-Ji Liu, Motorola Advanced Systems Research Laboratory, Mesa, AZ.

Ta has been used as a diffusion barrier for Cu interconnect technologies. In this study, we account for the presence of Cu in the Ta seed layer on Ta barrier by sputtering is fine-grained due to the nature of the nucleation process. Grain boundaries in the Ta seed layer may have become one of the sources of vacancies for Cu to diffuse across the Cu/Ta interface into Ta. Another potential source for vacancies is sputtering itself. The kinetic energy of Cu ions for ionized Cu PVD process is typically capable of creating vacancies at Ta surface. In this work, we calculated defect formation and migration energies in Cu and Ta, including Cu migration energy in Ta and Ta migration energy in Cu. The results indicate that with vacancies readily available at the Cu/Ta interface, Cu diffusion into Ta is more rapid compared to Ta diffusion into Cu. The calculated results support previous experimental observations. A brief discussion on how a dopant can be added to the Cu seed layer or the barrier layer to slow down Cu diffusion will also be given.

03.3 PHOTOACOUSTIC SPECTRA FROM COPPER-PHTHALOCYANINE FILMS ON SILICON WAFER.
Masaaki Onohsaki, Hiroshi Kubota, Yasuo Tsutsumi, Akashi College of Technology, Akashi Hyogo, JAPAN.

Copperphthalocyanine is attractive as an organic material for electronic and optical use. When the material is deposited on silicon, the optical absorption cannot be measured. We then obtained photoacoustic spectra by a copperphthalocyanine films deposited on silicon wafers and investigated absorption properties non-destructively.

03.4 SHAPE AND MICROSTRUCTURE IN ELECTRODEPOSITED COPPER: SUPERCONFORMALITY-FILLED 500 TO 75 NANOSTRUCTURE FEATURES. Daniel Joel, Thomas Moffet, Daniel Wheelier, John Rosenzweig, William Hallet, Gary Stafford and David Kelly, National Institute of Standards and Technology, Gaithersburg, MD. Andrei Stroehovski, Institute for Plasma Research, Department of Physics, University of Maryland, College Park, MD.

We identify an electric yields superconformal electrodeposition of copper in trenches ranging from 500 to 90 nm in width (all 500 nm deep), a unique hysteresis response in the current-voltage (i-V) deposition characteristics of the 'superfilling' electrolyte, and a 33% decrease of the resistivity of the electrodeposited copper in less than one day at room temperature. Trenches as small as 75 nm wide and 250 nm deep were also filled. Superconformal electrodeposition was obtained using an acid cupric sulphate electrolyte containing chloride (C1), polyethylene glycol (PEG), and 3-Mercapto-1-propanesulfonate (MPSA). In contrast, deposition of copper from nonfilling electrolytes containing the binary combinations C1PEG or C1MPSA, or simply benzoic acid yielded a continuous void within the centers of the trenches. A large hysteresis in the i-V deposition characteristics is associated with the 'superfilling' C1PEG-MPSA electrolyte and can be utilized to monitor and explore additive efficacy and consumption. Resistivity measurements performed on corresponding blister films were used to quantify the relationship between the extent of additive incorporation and its influence on microstructural evolution. Trenches deposited from the 'superfilling' C1PEG-MPSA electrolyte exhibit room-temperature recrystallization that results in a 23% drop in resistivity within a few hours of deposition. Reduction of void volume found during conformal deposition from the nonfilling electrolyte through combination of geometrical leveling effect for trenches with sloping sidewalls and more rapid deposition at trench openings is also demonstrated. These relevant have been compared with those of trenches with sloping sidewall because they were the best materials available. However, it is perhaps of greater interest as an intentional mechanism for obtaining improved filling of trenches and void, e.g., from electrolytes that do not provide perfect fill but might be desirable for other reasons.

03.5 A STUDY ON THE UNIQUE CRYSTAL MASTEY ORNAMENT OBSERVED IN THE POLYCRYSTALLINE COPPER CVD PROCESS. Yunjung Chang, Yalin Chen, Kukhun Chen Luoyang Institute of Technology, Dept. of Chemical Engineering, Guyangshan, Tsuyuyan, Taiwan, R.O.C.

In this presentation, we will show characterization results from copper whisker growth phenomena observed in an atmospheric pressure CVD. This CVD process used copper acetylecetone, Cu(C6H4O2)2 as precursor, and H2O vapor as a reducing agent. The products, chromium acetylacetonate, Cr(C6H4O2)3, introduced as activating catalyst reactant, at deposition temperatures exceeding 400°C. SEM and XRD observations show that introduction of 0.08 torr of Cr(C6H4O2)3 vapor into depositing chamber, with H2O pressure above 10 torr, caused polycrystalline Cu[111] and [200] to evolve whisker morphology. The whisker length ranged from 1 to 10 μm, with a surface distribution density of 0.26323/μm2. When deposition temperature raised, the length and radius of whisker increased, but surface distribution density decreased. Also, increasing H2O partial pressure caused the length and radius of whisker to become larger. By applying Arrhenius equation onto whisker growth rate to deposition temperature data, we have performed calculations showing the growth activation energies for whisker in axial direction are 120 kcal/mol and 12 kcal/mol in radial direction. Based on such data and SEM micrograph observations, vapor-liquidsolid (VLS) model describing controlling mechanisms for film microstructure was proposed. We employed this model to interpret competitive growth for both directions, and tentatively defined the axial direction whisker growth being the reaction controlled, and radial direction being mass transfer controlled.


Film deposition processes employing remotely generated plasmas to deliver reactive species to a substrate, such as ion beam assisted deposition (IBAD) or inductively coupled reactive plasma (ICRP) enhanced deposition, are recognized for their ability to increase deposition rates and modify the (micro- and/or lattice) structure of thin films. Manipulation of extrinsic process conditions such as gas flow, power, etc. in IBAD and ICRP processes produces measurable changes in intrinsic process conditions such as ion and electron energy distributions and densities. Intrinsic deposition conditions, when correlated to film properties, yield useful information about processing/structure/property relationships. This information continues to be an important factor in the design of our deposition processes and equipment. For example, we can measure the react ion density and energy distributions of the ICRP and ion beam sources. By varying the source gas composition and power conditions it is possible to optimize the number density (for maximum deposition rate) and energy distributions (for desirable film microstructure) of all species present in the chamber. It is evident from the measurement of intrinsic conditions that the behavior of the reactive sources is such that an optimization of this kind would be difficult to achieve using an "intuitive" approach, in which one makes educated guesses about optimum extrinsic processing conditions, and that plasma diagnostics facilitate intelligent process design.
O3.7  
**VOLTAGE INFLUENCE ON SURFACE MORPHOLOGY OF TITANIUM NITRIDE SYNTHESIZED BY DYNAMIC NITRATION AND TITANIUM PLASMA ION IMPLANTATION AND DEPOSITION.** Xiaoxian Tian, Langping Wang, Kingyu Fu, Paul K. Chu, Dept of Physics & Materials Science, City University of Hong Kong, HONG KONG.

Titanium nitride thin films are synthesized on AISI 304 stainless steel substrate using dual titanium and nitrogen plasma in an immersion configuration. The titanium plasma is produced by a vacuum arc plasma source whereas the nitrogen plasma is sustained by hot filaments glow discharge. A 30 microsecond implantation duration and 270 microsecond titanium nitride duration are used to have both ion implantation and metal deposition. The impact of the implantation voltage on the film morphology is investigated using three voltages, 8kV, 16kV, and 24kV. Atomic force microscopy analysis reveals small islands with polygonal shape and the 8kV sample is relatively smooth and more or less uniformly distributed on the surface. The surface morphology of the higher voltage samples is quite different. The density of the surface islands decreases but they become higher and steeper. On the 24kV sample, the hillocks become less uniform and appear like clusters of arrows. In addition to presenting the experimental results, we will discuss the mechanism by describing the impact of the implantation voltage on the growth dynamics of the coating and the relevant ion bombardment effects.

O3.8  
**Tlₓ₋ₓ W N FILMS WITH DIFFERENT TUNGSTEN CONTENTS.** Ayako Kimura, Hiroyuki Hasegawa, Tetsuya Sasaki, Keio Univ, Dept of Mechanical Engineering, Yokohama, JAPAN.

Addition of second metals such as Al, Zr and Cr into TiN films substitutes some Ti atoms with these metals and provides higher hardness and improvement of wear resistance. For example, the crystal structure of [Ti,Al]N is kept cubic but the lattice parameter decreases in proportion to the content. For the practical purposes such as cutting tools and molds, there are many reports on [Ti,N]N, [Ti, Zr,N] and [Ti, Cr,N] films based on hardness and wear resistance. On the other hand, few studies have been reported on [Ti, W]N system because of experimental difficulties, although more attractive properties have been expected. In this study, we prepared Tiₓ₋ₓ W N (0 ≤ x ≤ 1) films using Ti and W targets by the arc ion plating method changing W contents. In this method, atoms or clusters ejected from surface of targets, are ionized and reacted with process gases, and finally reach substrates as films. The Ti and W targets were simultaneously arc-discharged at an arc current of 0 - 100 A in order to change W content in Tiₓ₋ₓ W N films. The films were deposited on cemented carbide substrates which were biased at 20 V and at temperature of approximately 500°C under nitrogen plasma circumstance. After the film deposition, micro-hardness of films was measured by the conventional micro-Vickers hardness test comparing with the hardness of the film synthesized novel Tiₓ₋ₓ W N films by changing the W ratio against Ti and measure their mechanical properties. Further, we discuss the potential use of Tiₓ₋ₓ W N films for practical purposes.

O3.9  
**A STUDY OF THE INTERACTIONS GUIDING THE FORMATION OF LAYER-BY-LAYER FILMS.** Maria Rospo, Paulo António Ribeiro, Universidade de Lisboa, Faculdade de Ciências, Departamento de Física, Lisboa, PORTUGAL; Nara C. Souza, Osvaldo N. Oliveira Jr, Universidade de São Paulo, Instituto de Física de São Carlos, São Carlos, SP, BRAZIL.

The formation of layer-by-layer films is mainly based on electrostatic interactions since they are the result of polyelectrolyte adsorption from solution onto electrically charged surfaces. However, depending on the polyelectrolyte structure, interactions as layer-by-layer formation can also play an important role in the film formation and consequently in the properties of a final device. In order to investigate the interactions responsible for the film cohesion a thermally stimulated desorption technique in solution was employed. In this technique, the temperature of the film solvent system is increased at a constant rate and the amount of desorbed material measured as a function of the temperature. Desorbed amount rate versus temperature curves reveal peaks from which activation desorption energies can be determined. Activation desorption energies of 75 kJ/mol and 220 kJ/mol were obtained in layer-by-layer films of poly(o-methoxyatylene) (POMA) alternated with poly(vinylsulfonic acid) (PVS) terephthalic acid (PVT) trisulfonic acid. The presence of hydrogen bonding is the explanation for the adsorbed amount to be dependent on the concentration, in opposition to what can be expected from the adsorption of changed polymeric molecules onto a layer onto a layer-by-layer film should be dependent on the number of electrical charges of the last adsorbed layer and, as a consequence, independent of the polyelectrolyte concentration.

O3.10  
**EVOLUTION OF INTERFACE DURING TOP FILM DEPOSITION: DIFFERENCE IN SURFACE ENERGIES.** Victor Popovshchik, Recording Head Operations, Seagate Technologies, Minneapolis, MN.

A Monte Carlo simulation has been used to study how the difference in surface energies of the deposited films affects the stack structure. This simulation indicates that each film can considerably change the interface geometry and even the structure of the bulk. More specifically, it has been shown that: 1. Deposition of a film with higher surface energy upon a film with lower surface energy can lead to significant roughening of the interface. Thus, in stacks, interface morphology can be very different depending on the deposition order. 2. The atoms of the bottom film having low surface energy tend to float up and the atoms of the top film tend to dig into the first film. This effect can be reduced by increasing the surface roughness of the boundary layer. The model shows that the growing surface should be maintained. In the result of the simulation, the system gets through the roughening. 4. Because surface diffusion is much faster than volume diffusion, segregation at the growing surface should be much easier than in the bulk. Therefore, the described phenomena took place until the second film has covered the first film completely. 5. Negative mixing energy (the components do not want to mix) suppresses the interface roughening. 6. The predictions of the model are in agreement with the experimental evidence on the effect of difference in surface energies on film growth.

O3.11  
**Abstract Withdrawn.**

O3.12  
**REDUCED ORDER REPRESENTATIONS OF EPITAXIAL THIN FILM GROWTH.** Martha A. Gallivan, David G. Goodwin, and Richard M. Murray, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

Control of epitaxial thin film deposition processes requires a model that can predict, at least approximately, the change in film properties of interest resulting from changes in process conditions. For epitaxial films, kinetic Monte Carlo models are often used to simulate the evolution of surface morphology, but KMC models are usually too slow to run in real time, as required for control applications. Furthermore, most control strategies require that the system be described by a set of ordinary differential equations. We are investigating methods to simplify KMC models and generate approximate ODE models that can be incorporated into real-time control applications. A possible method is to determine a set of measurable quantities as a result of a paper reporting on the mathematical modeling of the film response of measurable output data (e.g., roughness, RHEED signal) in changes in process conditions predicted by KMC. We begin by casting the KMC model into a linear system of ODEs, albeit with very high dimension. We then attempt to reduce the dimensionality of the state space permitted (e.g., through model reduction, e.g., via proper orthogonal decomposition (POD)). Standard techniques to reduce the dimensionality of large systems of linear ODEs are available, and here we explore their use to generate highly reduced ODE models that capture the important temporal and spatial features. The main factors which influence the shape of POD's and correlation functions are determined and...
possible connections between the constitution of the polycrystalline template (e.g., shape and size distribution of the crystalline domains) and the film roughness are discussed.

03.14 ANGULAR DEPENDENCE OF THE DYNAMICAL SCALING BEHAVIOR IN LOW-MOBILITY MODELS OF THIN-FILM GROWTH. Jianguo Yu, Jacques G. Amar, Univ of Toledo, Dept of Physics & Astronomy, Toledo, OH.

We have studied the dynamical scaling behavior as a function of the sputter-angle distribution in two- and three-dimensional models of ballistic deposition with shadowing. In particular, we have studied two different distributions, a uniform angular distribution corresponding to high Ar pressure and a cosine-like angular distribution corresponding to low or moderate Ar pressure. While in all cases, the resulting films are compact, in two-dimensions we find that there exist two distinct universality classes described by different values of the commensuring and renormalizing exponents. The characteristic behavior of the fractal feature size and surface roughness with film thickness, as well as of the surface fractal dimension $D_f$, in order to accurately determine the surface fractal dimension a novel dynamical scaling form was used. For the case of a uniform distribution we find $p = 2/3$ and $D_f = 1.7$ while for a cosine distribution we find $p = 3/2$ and $D_f = 1.5$ while the roughening exponent $\beta$ depends on microscopic details. In contrast, an angular distribution corresponding to a narrow range of angles with respect to the substrate normal leads to a self-affine surface. We conjecture that the scaling behavior depends on the exact form of the angular distribution but depends primarily on the large-angle behavior. This is confirmed by results obtained for other angular distributions. The behavior of surface diffusion and shadowing with varying $\beta$ will also be discussed. Results for the case of three-dimensional ballistic deposition with both a cosine and uniform distribution will also be presented.

03.15 NANOGRAPHIC STUDIES OF Cu/Cr AND TiB$_2$/Cu/Cr MULTILAYERS AT THE NANO- AND MICROSCALE. G. Wei, J. De, A. Bar, and J. A. Barnard, Department of Metallurgical and Materials Engineering and Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, AL.

The nangographic behavior of de magnetron sputtered Cu, Cu/Cr, TiB$_2$/Cu and TiB$_2$/Cu/Cr deposited on Si(100) has been studied using nanoindentation and nanoscratch techniques. The hardness and modulus of the thin films were measured by a Hysitron nanomechanical testing system. Constant and ramped load scratches were made using a Nano Indenter II system at various loads (300N, 1000N and 10000N). X-ray and X-ray reflectivity were used to measure the film structure and film thickness, respectively. Atomic force microscopy was used to evaluate the surface morphology and the scratch wear tracks of the films. The grain size and orientation of the Cu thin films were measured by TEM. To analyze the influence of Cr underlayer on Cu and TiB$_2$/Cu thin films, the hardness of Si(100) substrate and Cr thin films were both measured. Although the hardness of Si (about 11-15 GPa) is higher than Cr (about 8-10 GPa), the hardness of Cu/Si or Cr/Si or Cu/TiB$_2$/Cu/Si or Cr/TiB$_2$/Cu/Si respectively, indicating that the 2 nm thick Cr underlayer may change the growth of the Cu thin films deposited on it. AFM images show that the roughness of Cu/Si thin films (1.34 nm) is lower than Cr/Si (2.67 nm) or Cu/TiB$_2$/Cu/Si (2.60 nm). X-ray diffraction patterns also indicate that the structure of Cu has been changed when deposited on the Cr underlayer. In the nanoscratch tests, the Cu and TiB$_2$/thin films with Cr underlayers present higher critical load than the ones without Cr underlayers. For each of the four films, under the same load, the displacement in constant load scratch is higher than in the ramped load scratch. The mechanism responsible for this difference in displacement has been analyzed.

03.16 LEVEL SET SIMULATION OF 3-D POLYCRYSTALLINE FACETED FILMS. Xiangdong Li, Dept. of Physics, University of Michigan, Ann Arbor, MI; David J. Srolovitz, Princeton Materials Institute, Princeton University, Princeton, NJ; Giovanni Russo, Dept. of Mathematics, University of L' Aquila, ITALY.

We have developed a general purpose algorithm for the growth of polycrystalline films, faceted thin films from the vapor based upon the level set method. The variation of the film microstructure and morphology with growth rate, temperature, and composition of the reactive crystalline facets will be examined. The evolution of grain size, texture and surface roughness with film thickness will be presented. We will also present our simulation results on the growth of polycrystalline films in the presence of a low energy ion-beam, which is used to establish in-plane texture. We examine the development of the film microstructure and in-plane texture as a function of ion beam properties.

03.17 STUDY OF ATOMIC STEPS ON THE SINGLE CRYSTAL SURFACE BY GRAZING ION SCATTERING. Abrhaer Dahshan, Institute of Electronics, Tashkent, Uzbekistan.

Ion bombardment of a solid surface leads to radiation-induced vacancy defects, atomic steps and their clusters, as well as the atomic scale relief formation. The concentration and the type of the radiation defects being formed depends upon the experimental conditions and significantly influences the trajectories, angular and energy distributions, as well as the number of the scattered particles. In the present study the low-energy Ne and Ar ion scattering from atomic steps on Cu[100] and GaP[100] surface at grazing incidence, their deflection effects have been investigated by computer simulation. The trajectories of the particles scattered both by the ordered part of the surface and the monoatomic steps of the different spatial extension phased upon it have been carefully studied in the binary collision approximation using the universal Biersack-Ziegler-Littmark interaction potential. Elastic and inelastic energy losses have been summed along the particle path. Energy distributions of particles scattered by the isolated monoatomic steps [fragments] consisting of several atoms (from one to four) have been calculated. The distances between the steps vary from two lattice constants to 50 A. The characteristic peaks in the energy distributions were explained by the features of trajectories of scattered particles. Comparison of calculated and experimentally measured energy spectra showed that the most likely ones turned out to be steps [fragments] consisting of two and three atoms separated by the parts of the ordered surface of the length 15-55. It has been shown that, from the correlation of the experimental and calculated energy distributions of the scattered particles, one may determine a spatial extension of the isolated atomic steps and distance between them on the single crystal surface damaged by the ion bombardment. The deflection of ions from the monatomic step was effective in ion scattering on the GaP[100] surface as well as on the trajectories of these particles have been carefully studied. The energy and angular distributions of the deflected ions were calculated. It was shown that the deflection ions form the characteristic peaks in the angular and energy distributions of scattered ions. The deflection mechanisms of particles moving under surface atomic steps are discussed.

03.18 DEPOSITION OF Ru THIN FILMS PREPARED BY MOCVD USING DIRECT LIQUID INJECTION SYSTEM. Sang Yeol Kang, Cheol Seong Hwang, Hyojeong Joon Kim, Seoul National University, School of M&ISE, Seoul, KOREA.

The requirements for the chemical vapor deposition (CVD) of metal films for the (Ta$_2$O$_5$)/SiO$_2$/ [BST] capacitor of dynamic random access memory (DRAM) devices becomes more critical as the storage node height increases. With the three dimensional geometry of the capacitor, the plate electrode need to be deposited by CVD as otherwise the device may suffer from a reliability problem due to electrical leakage or chemical corrosion. One common method to deposit a thin conformal Cu/Si thin films (100 nm) is to use a combination of MB, and B, and SiC. XRD diffraction patterns also indicate that the structure of Cu has been changed when deposited on the Cr underlayer. In the nanoscratch tests, the Cu and TiB$_2$/thin films with Cr underlayers present higher critical load than the ones without Cr underlayers. For each of the four films, under the same load, the displacement in constant load scratch is higher than in the ramped load scratch. The mechanism responsible for this difference in displacement has been analyzed.

03.19 SURFACE INDUCED CHEMICAL ORDERING OF [001] FePd EPITAXIAL LAYERS GROWN BY MOLECULAR BEAM EPITAXY. D. Halley, Y. Sunan, A. Marty, C. Beigne, CEA/DMF/IEGEM, Grenoble, FRANCE, B. Gilles, CIRN/ITPM, Grenoble, FRANCE.

We investigated the ordering of equiatomic FePd epitaxial films deposited by MBE on Pt [001]. This alloy shows an ordered tetragonal CuAu I type structure (L1$_0$), which is known to exhibit a considerable interest due to its magnetostructural response along the c-axis. Growth at room temperature yield disordered films, whereas growth at 300° C yield well ordered FePd alloys with the c-axis oriented in the growth direction, leading to a tetragonal lattice. We find that the ordered FePd planes parallel to the surface. By scanning tunneling microscopy on the surface of ordered films we observed mono and bi-atomic steps. As Elsinga and Lagerlof have reported, low energy ion bombardment of FePd was pure Pt, due to segregation, we evidenced that bi-atomic steps
reflect the ordered structure of Fe-Pd bilayers, whereas monotomic 
steels might be the emergence of multiple phases within the L10 
phase. This behavior is explained by the lack of sufficient 
interatomic layers during growth: the period corresponds to one atomic 
monolayer in the case of disordered films, and to two atomic layers in 
the case of ordered films. Moreover, disordered films grown at room 
temperature and next annealed for hours at 650 K (10) exhibit along the 
c-axis along the three (100) directions, contrary to films grown at 
620 K. It suggests that the uniaxial orientation during growth is driven by 
surface processes, outlined by the formation of bi-atomic steps, the segregation nuclei of the c-axis, and the emergence of 
Growth at intermediate temperature, between RT and 620 K lead to 
partial ordering by the same c-axis. Observation of these samples by 
TEM and X-Ray evidenced a pseudo-periodic arrangement of 
the disordered domains having a columnar shape whose size might be set 
by diffusion length along the straight growth.

03.20 
CHEMICAL ORDERING AND MICROSTRUCTURAL 
DEVELOPMENT IN NICKEL ALUMINIDE THIN FILMS. Gregory B. Thompson, Rajeshri Bonerjee, Peter M. Anderson, Hamish L. 
Frazer, Dept. of MSE, Ohio State University, Columbus, OH.

Thin films of alloys and intermetallic compounds are finding 
increasing applications as structural components in the aerospace, 
microelectronics and magnetic recording industries. An interesting 
candidate for such coatings is the chemically ordered intermetallic 
compound Ni$_3$Al which has been extensively researched in the bulk 
form. This paper describes a novel study of the microstructural 
behavior of sputter-deposited polycrystalline thin films of Ni$_3$-25Al 
as a function of substrate temperature. Films were deposited on oxidized Si substrates at ambient temperature, 423 K, 
and 673 K. These films have been characterized by x-ray diffraction 
and transmission electron microscopy. The film deposited at ambient 
temperature exhibited an ordered structure and a columnar grain morphology. However, in contrast to the behavior of 
sputter-deposited elemental metals, the films deposited above ambient 
temperatures consisted of refined microstructures and exhibited a 
lower degree of texturing. This anomalous behavior has been explained by the role of exothermic heating accompanying chemical ordering and 
consequent formation of the L1$_2$ Ni$_3$Al phase in the film.

03.21 
EPITAXIAL GROWTH AND INTERFACE ROUGHNESS OF 
Nd$_3$Mn$_8$Fe$_3$ BILAYER STRUCTURES GROWN BY ION-BEAM 
SPUTTERING. Ning Cheng, Materials Science and Engineering 
Department, University of California Berkeley. Werner Grogger, J.P. 
Ahn and Kannan Krishnan, Materials Sciences Division, Lawrence 
Berkeley National Laboratory, University of California, Berkeley, CA.

Epitaxial Nd$_3$Mn$_8$Fe$_3$/MgO bilayer structures were grown by IBS (ion 
beam sputtering) at different substrate temperatures. Different 
orientations of Nd$_3$Mn$_8$Fe$_3$ and different stacking orders of Nd$_3$Mn$_8$Fe$_3$ 
and Fe on MgO(001) were studied. The interface roughness of these 
samples was characterized by energy-filtered transmission electron 
microscopy (EFTEM). The orientation relationships were confirmed by 
x-ray diffraction and TEM. The final Nd$_3$Mn$_8$Fe$_3$ orientation 
determined by the competition between the growth kinetics and 
thermodynamic parameters. At low temperatures (T<280°C) dominated 
by the kinetics of growth, a (001) oriented 
Nd$_3$Mn$_8$Fe$_3$(100)/Fe(001)/MgO(001) was stabilized whilst a 
Nd$_3$Mn$_8$Fe$_3$(110)/Fe(001)/MgO(001) was deposited at temperatures (T>380°C) when the thermodynamics forces domain. 

03.22 RELATION BETWEEN TEXTURE AND STRESS IN THIN 
MOLYBDENUM LAYERS. Ilse M. van den Berk, Lien J. Scijne, 
Bob Delhez, Laboratory for Metallurgy Science, Delft University of 
Technology, Delft, NETHERLANDS.

Pure Nb layers were deposited by magnetron sputtering at room 
temperature on an oxidized silicon wafer (100) at four sputtering 
pressures: 0.25 Pa, 0.5 Pa, 1 Pa and 2 Pa. The thickness of the deposited layers is 550 nm, the deposition rate was 
16.7 nm/min at a power of 510 W (DC). X-ray diffraction was used to evaluate the stress and texture of the layers. All specimens show an 
almost perfect (111) orientation. A more or less uniform texture across the entire film thickness also show a preferred in-plane orientation with (110) 
planes perpendicular to the rotation axis of the sputter table. The sin²(2θ)-method was used to determine the stress in the layers. By measuring the strain along the (110) orientation, the stress was determined as 
sensitive and not rotationally symmetric. Heat treatments at 600 and 
800 K were performed on the layer deposited at 0.5 Pa. It was found that stress decreases in the textured layer. The absolute magnitude of the stress in the layer decreased indicating a decrease of the intrinsic 
or growth stress. At the same time the (110) orientation fixed and the stress in the plane became more rotationally symmetric. This paper explains the difference in stress and texture in relation to the sputter pressure.

03.23 MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF 
INTERMEDIATE RARE-EARTH METAL LAYERS FOR 
MEDIUM-K DIELECTRIC APPLICATIONS. Nabil D. Baisan, V. 
Cracius, J. Howard, R.K. Singh, Department of Materials Science & 
Engineering, University of Florida, Gainesville, FL.

The development of high-K dielectric materials to replace SiO$_2$ as 
the gate oxide in silicon-based MOS device structures has attracted 
much interest recently. One of the key challenges in producing thin-film 
films has been to prevent the formation of an interfacial layer of SiO$_2$ 
between the film and the substrate, which subsequently reduces the 
effective gate oxide capacitance. One possible solution to this problem is to use a dielectric interfacial layer that is more stable than the 
substrate SiO$_2$, and which, when unalloyed in an oxygen 
ambient, can form a thermodynamically stable very thin rare-earth 
silicate or oxide layer. Films were unalloyed in a nitrogen 
ambient atmosphere to form a stable silicate layer and SiO$_2$. The films were subsequently deposited in order to have the same 
value of the SiO$_2$. Cross-sectional high resolution transmission electron 
microscopy and x-ray photoelectron spectroscopy were used to 
investigate the layers formed in this composite structure and the 
microstructure and processing parameters were related to the measured Capacitance-Voltage and Current-Voltage characteristics of the film.

03.24 TEXTURE IN THIN FILMS. Nb/Al, Ti/Al AND Al. 
Wayne Archibald, Kazuyama Bormak, Carnegie Mellon University, 
Dept. of Materials Science and Engineering, Pittsburgh, PA; Gene 
Lucadamo, Lehigh University, Dept of Materials Science and 
Engineering, Bethlehem, PA.

Texture in Ti/Al and Nb/Al polycrystalline multilayer thin films, 
with bilayer thicknesses ranging from 20 to 333 nm and having a fixed 
stacking geometry of 1/8, and pure Nb and Al films 300 to 1000 nm 
thick. The films were prepared at temperatures from 0.25 to 1 micron, has been investigated using x-ray pole figures and 
transmission electron microscopy. Two types of multilayer films were 
deposited, one set contained pure Al and the other AL-10 weight 
percent Cu. The texture was found to be strengthened by the formation of a coherent superlattice for the Nb/pure Al film with the 
smallest bilayer thickness. By contrast, the texture in Ti/pure Al 
films with a similar period was not as strong. The strength of texture 
only increased with increasing bilayer thickness for high Cu bilayer 
films. A high-Cu bilayer in producing high Cu bilayer pure Al films, the strength of texture was found to increase with 
increasing thickness. Near <111> fiber texture was observed in all cases. The results of our investigations were interpreted in the context of structure zone and dynamic roughness models of film growth.

03.25 MICROSTRUCTURE EVOLUTION OF ELECTROPLATING 
DEPOSITED NICKEL AS A FUNCTION OF PROCESSING 
PARAMETERS. Kun Liu, Center for Advanced Microstructures and
Electropolished Ni is the major material used currently in Microelectromechanical Systems. In the past, very little work has been done to study the relationship between Ni electropolishing parameters and resulting microstructures. The present work is focused on the processing-structure-technical property relationship of electropolished Ni. A sulfamate bath was used to produce Ni electropolishing temperature and current density were varied between 3.7°C-50°C and 5 mA/cm²-30 mA/cm², respectively to produce 50 μm thick Ni layers with a grain size ranging from 70 nm to 100 nm. The structures of the layers produced at the various processing conditions were characterized by cross-sectional TEM. Nanoindentation tests were conducted to assess hardness and elastic modulus of the Ni layers. Pin-on-disc experiments were performed to study the tribological behavior. The relationship between grain size and mechanical properties is discussed.

O3.26 CRYSTALLOGRAPHIC AND MORPHOLOGICAL PROPERTIES OF MAGNETRON SPUTTERED Ti AND Zr THIN FILMS
Ellaine F. Cunningham, Ivette C. Oppenheim, University of Sao Paulo, Institute of Physics, Sao Paulo, SP, BRAZIL.

The microstructure of polycrystalline hcp Ti and Zr thin films was analyzed with Atomic Force Microscopy and X-ray Diffraction. The films were deposited by magnetron sputtering on amorphous substrates (SiO₂ over Si). The used Ar gas partial pressure and the deposition rates were 0.8 mTorr and 0.08 mTorr, respectively. The surface morphology and crystallographic properties of the films were studied as a function of the homologous temperature (T/Tₘ)0.43, where T is the substrate temperature during deposition and Tₘ is the melting temperature of the film material. The thickness (40 nm ≤ 278 nm). At low temperatures (T/Tₘ) = 0.15, Ti and Zr films have an (0002) preferential texture. The texture and the crystalline grain sizes do not depend on the thickness of the films. As a consequence of low surface diffusion and grain boundary mobility, the surface morphology is composed by small grains and compact grain boundaries. The well-defined crystallographic texture suggests that the initial nucleation is formed by islands with preferential orientation. At T/Tₘ ≤ 0.43, the texture of the Zr films improves. The higher the temperature, the thicker the films that present a dominant (0002) preferential texture. For the Ti films, as T/Tₘ increases, the (0002) texture decreases giving rise to a (101) texture. At T/Tₘ = 0.43, the Ti films present a dominant (101) texture. In general, increasing the deposition temperature leads to an increase in the average grain diameter, and in the film thickness increases, the texture improves and the crystalline grain sizes increase. The growth rate of the average grain diameter as a function of thickness is higher for the Ti films than for the Zr films. The evolution of surface morphology and texture of the films suggest that the Zr films present an almost columnar structure while the Ti films are formed by grains with a cone-like shape as a consequence of competitive grain growth.

O3.27 COMPARISON OF THE ATOMIC PEENING EFFECT IN SPUTTER-DEPOSITED EPITAXIAL AND POLYCRYSTALLINE Pt/Pt MULTILAYERS
V. Ramaswamy, W. Nix, and B. M. Clemens, Stanford University, Dept. of Materials Science and Engineering, Stanford, CA.

Energetic bombardment of films during sputter deposition by reflected neutral gas atoms (typically Ar) and target atoms, also known as atomic peening, has a pronounced effect on film stress and microstructure. The bombardment energy, and hence the degree of peening, decrease in sputter gas pressure is increased, due to increased thermal energies. Differences in stress generation due to atomic peening in polycrystalline and epitaxial layers are studied using in situ substrate curvature measurements during sputter deposition of Pt/Pt multilayers. Coherence stresses, based on bulk lattice mismatch, are compressive for Pt and tensile for Pt. Stress behavior of Pt layers in epitaxial and polycrystalline samples is similar; at low Argon pressures, large compressive stresses consistent with coherent and atomic peening develop in the Pt layers. At high Argon pressures, Pt layers are in tension after initial coherence-related compressive behavior. The behavior of polycrystalline and epitaxial Pt layers, however, are markedly different. While some peening-related compressive stress is observed in polycrystalline Pt at low Argon pressures, the initial Pt layer layer has compressive behavior. The peening-related compressive stress sustains high tensile stress, likely due to coherency, and is insensitive to changes in sputtering gas pressure. This difference in stress behaviors of epitaxial and polycrystalline Pt is attributed to large microstructural changes in the layers. Observed stress behaviors in Pt and Pol are discussed in terms of simple microstructure, and surface morphology. A simplified one-dimensional diffusion model for defect incorporation during thin film growth provides useful insight into the atomic deposition parameters and material properties related to the atomic peening effect.

O3.28 THE STAGES OF STRUCTURE-ENERGETIC TRANSFORMATIONS AT COMBUSTION SYNTHESIS IN THE SYSTEMS
NIA AND TAI: M. D. Starostin, Gennady M. Polteyev, General Physics Dept, Altai State Technical Univ.

It is known that combustion synthesis (CS) takes place at high velocities. That is why it is difficult to determine the stages of structure-energetic transformations, taking place at CS. The process of CS is modeled by the Gurney and other dynamical methods. The investigating systems are presented in a form of metallic thin films at the beginning of the process. The interactions between the atoms are given by the sets of empirical pair potentials. The investigated critical parameters, simulating the velocity of the transformation of CS is found in the result of computer experiment. The parameters are the following: limited free volume, its connection with the temperature of the process beginning, the velocity of components mixing, the velocity of formation of intermetallic phases. It is established, that the structure transformations of the system take place at the formation of micrometallic phases in the process of CS.

O3.29 MICROSTRUCTURE ORIGIN FOR THERMAL FATIGUE OF TiNi FILMS.
Shulin Wen, Shandong University, Dept of Material Science and Engineering, Shandong, CHINA.

Fatigue is a progressive and localized permanent structural change. It occurs in such a material which subject to repeated and fluctuating stress. Fatigue occurs in TiNi shape memory alloy (SMA) during its application due to repeated and fluctuating stresses at low/high temperature cycling. One of the goals of TiNi SMA application is to make miniature valve in smart microvalve which is applied to combustion engine or closed-loop control drug delivery system. The material used for this purpose needs to work for millions of low/high-temperature cycles at least. Fatigue then occurs and the decay of the performance of SMA first and then further fractures produced. Therefore it is very important to investigate the microstructural origin of this fatigue in order to retain the SMA performance as long as possible in life. The parent phase in present TiNi films has B₂ structure, on cooling it may transform martensitically to B₁₂' and B₁₂ phases. Present investigation results showed that a small amount of B₂ phase did not transform to B₁₂' and B₁₂ phases due to dynamic release and a little amount of H phase formed. This martensite transformation. Present investigation also indicated that there some precipitates produced in the fatigue specimens. The precipitates which are responsible for the fatigue were observed in the fatigue specimen as truce phase with grain size of 10-20 nm. It could be identified as TiNi₁ phase from our TEM image, electron diffraction pattern and EDX analysis result. To effectively control the precipitates is the key to improve the SMA film performance.

O3.30 MICROSTRUCTURE, STRESS AND MECHANICAL PROPERTIES OF ION BEAM SPUTTER DEPOSITED, METAL HYDRIDE THIN FILMS.

We investigate the microstructure, stress and mechanical properties of reductively sputter deposited metal hydride thin films. Metal hydride films are currently of interest for microfluidic cells, dough-hole oil logging devices and switchable mirrors. In present work, the development of metal hydride film microstructure is studied as a function of the deposition conditions. This includes analysis of crystal texture and phase for rare earth metal hydride compounds, including samarium hydride. Films are deposited onto several different substrates (Si[100] having native oxide, molybdenum, stainless steel, and stainless steel) in order to determine the influence of the substrate. Thin film stress is monitored during each stage of fabrication including nucleation, growth and post-deposition cooldown using a laser based, multi-beam wave curvature sensor. Stress developed during deposition is correlated with changes in morphology, microstructure and composition. Extrinsic stress is probed after deposition to accurately determine coefficients of thermal expansion. These results suggest that strain energy influences the stability of certain rare earth metal hydride crystal phases. Furthermore, we evaluate the mechanical properties of films using nanoindentation and nanoscrap techniques. These tests determine the elastic moduli and interfacial toughness of metal hydride films.

The work was performed at Sandia National Laboratories and is supported by the United States Department of Energy under contract no. DE-AC04-94AL85000. Sandia is a multiprogram laboratory.
operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

03.31 THE LASER-MOSSBAUER METHOD FOR SURFACE EVOLUTION AND THIN FILM MICROSTRUCTURE. Monica Szunerits, Duquesne University, Physics Department, Pittsburgh, PA.

The laser-Mossbauer method is a new method pioneered in our laboratory for the study of amorphous magnets and their microstructures. It is a new method, of a hybrid type: processing-characterization. The method combines an extremely sharp tool for exciting the amorphous structure with a characterization technique that has the highest resolution known to physicists. We shall demonstrate that this method yields amorphous magnets with controlled properties. Using amorphous Fe3B, FeNiMo3, FeCoBSi and FeCrAlSiY as model systems, we applied the laser-Mossbauer method in order to obtain magnetic and electronic properties of amorphous and nanocrystalline Mossbauer spectroscopy, the bulk magnetic texture was modified in a rational manner by applying a varying number of excimer laser pulses per spot. As shown by conversion electron Mossbauer spectroscopy (CEMS), this process left the surface magnetic texture unchanged and induced a distribution of magnetic moment directions through the thickness of the foil. A similar dependence of the magnetic texture on the number of applied laser pulses was observed in metallic glasses irradiated with a Nd:YAG laser. However, in this case we observed the onset of surface crystallization using the hyperfine magnetic field distributions extracted from the CEMS spectra. When a pulsed alexandrite laser was used, the onset of crystallization was found to be accompanied by bulk oxidation and the formation of magnetic nanoparticles in the irradiated system. Finally, a crucial experiment was performed in order to demonstrate the role played by the magnetostatic coupling constant in the onset of crystallization. Consequently, the laser-Mossbauer approach made it possible to obtain unique information on the surface evolution and thin film microstructure, as well as produce materials with new types of magnetic moment distributions, not obtainable by conventional methods.

03.32 THE FABRICATION, THE STRUCTURAL AND SURFACE STUDIES OF RARE-EARTH HEXAPOSEXIDEM THIN FILMS. Zhenchen Zhong, Institute for Micromachining (IM) and Physics Program, Louisiana Tech University, Ruston, LA, and Department of Physics, Grambling State University, Grambling, LA.

Rare-earth hexaboride Re6B (Re = Gd, Ce and Nd) thin films were fabricated by a novel laser-induced chemical processing Laser-induced deposition form solution (LSD). The Structures and Surface were studied by scanning electron microscope (SEM), X-ray emission spectroscopy (XES), and X-ray diffraction (XRD). We found that these films grow with a strong texture axis. The microstructure and surface of the deposited films were different even for coating the same film on the choice of solvents and laser parameters (e.g. wavelength, laser power etc.) used in LSD. Rare-earth hexaborides are typically low work function materials. They can be applied as cathodes in DC plasma display panels and micro-X ray tubes.

03.33 MOVCVD ZnMn FILMS: GRAIN SIZE DISTRIBUTION AND CRYSTAL STRUCTURE AS A FUNCTION OF THE GROWTH PARAMETERS. K. Dvodenko, K. Dunn, A. Topol, L. Senagasti, S. Oknyinsky and A.E. Kaloyeros, NYS Center for Advanced Thin Film Technology, the University at Albany-SUNY, Albany, NY.

Zinc sulfide doped with manganese is a promising material for thin film electroluminescence device applications. In order to fully assess the key material and process challenges, the ZnMn films were fabricated by the metagaphosphoric chemical vapor deposition on the Al2O3/InGaAs substrate, and the growth kinetics and correlation between the crystal structure and the electroluminescence performance were studied. The ZnMn films were grown in the 250~600°C temperature range, and fully characterized by the variety of structural and chemical characterization techniques such as Rutherford Backscattering, Secondary Ion Mass Spectroscopy, X-ray Diffraction, Scanning Electron Microscopy, Atomic Force Microscopy and Transmission Electron Microscopy (TEM). For all the growth conditions, the films were found to be polycrystalline having predominantly 2H hexagonal ZnS structure. The presence of the 2H crystal structure is detected with the low-temperature ZnMn films by the TEM, XRD and SEM techniques. The growth temperature and the gaseous compounds of the growth gas mixture are strongly correlated. The ZnS grains are found to grow columnar as the film thickness increases, also widening in the direction parallel to the substrate surface and reaching the 100-200 nm average lateral size at the 700 nm thick film. The characteristics of grain growth in the low-temperature ZnS layers: small-sized (average 2.5 nm) and large-sized (average about 50 nm measured at the 200 nm film thickness). For the high-temperature films, no grains smaller than 40 nm were observed, the average lateral size at the 700 nm film thickness was about 100 nm (measured at the film thickness of about 200 nm). The small-size grains in the low-temperature films were present all the way through the ZnS layer thickness with a little bit higher density at the ZnS/ATO interface. ZnS grains were attributed to the 8H hexagonal polytype. The correlation of the grain microstructure with the electroluminescence behavior is discussed.


The kinetics of surface morphology evolution of pulsed laser deposited strontium titanate (STO) homoeptaxial films was investigated by in-situ monitoring the influence of electron beam irradiation (REED) over a continuous annealing scheme. It was found that, independent of the temperature rising rate, an abrupt increase of REED intensity accompanied by the appearance of sharp diffraction spots always occurred near 600°C, indicative of a noticeable reduction of surface step density induced by surface morphology evolution. The temperature derivative of the REED intensity curve displays a resonance-like peak around 600°C, suggesting that a Longuinet-type force equation might be applicable in describing the kinetics. Analogies of the present observations to flux creep governed by individual pinnings are discussed.

03.35 THE INFLUENCE OF PLASMA COMPOSITION AND APPLIED POWER ON THE PROPERTIES OF PLASMA TREATED BIOMATERIALS. Nilsen C. Cruj, Elineir C. Rangel, Giovana Z. Cunha, Rogério P. Meira, Roberto V. Honda and Mauricio A. Agneti, UNESP - Campus Guaratinguetá, Dept of Physics and Chemistry, Laboratory of Plasmas and Applications, Guaratinguetá, SP, BRAZIL.

The response of a biological environment when in contact with an artificial material is primarily determined by material surface properties. Owing to this, different treatments have been employed to improve the performance of biocompatible materials. In this sense, plasma-based techniques are of particular interest because they enable the surface processing of materials with virtually any geometry, preserving bulk properties. In this work, glow discharge plasma and Plasma Immersion Ion Implantation (PHI) techniques have been applied in the treatment of metals (Ti and Ti6Al4V) and polymers (PTFE, ultrahigh molecular weight polyethylene and PMMA) largely employed in clinical and orthopedic devices. Plasma of inert (He and Ar) and reactive (O2, N2 and SF6) gases were generated in a vacuum chamber by applying radiofrequency power (13.56MHz, 300 W) to two external electrodes. In the PHI experiments the samples were biased with high voltage (2kV, variable frequency) negative pulses. The treatments were performed in different conditions of plasma composition and applied power. Nanodentation and pin-on-disc techniques were employed to evaluate hardness, friction coefficient, and scratch and wear resistances. An automated goniometer using the scratch method was employed to determine contact area and surface energy while elemental and structural modifications were determined by x-ray photoelectron and infrared reflectance-absorbance spectroscopies. It has been observed that the properties of the treated samples are extremely sensitive to plasma parameters. For instance, the contact angle of PTFE varied from 150 to 60 degrees when the oxygen partial pressure in the plasma ranged from 5 to 200 mTorr.

03.36 THE INFLUENCE OF PARTICLE FLUX DENSITY AND SUBSTRATE TEMPERATURE ON TEMPERATURE FORMATION IN TUNGSTEN CARBIDE ION-PLASMA CONDENSATES. Lilia I. Glabchik, Osg V. Scholl, Andrey Podolezhskiy, Kharkov State Polytechnical University, Dept. of Physics of Metals and Semiconductors, Kharkov, UKRAINE.

The energy E0 required to overcome the kinetic barriers for the atomic motion on a metal surface and to provide the occupation of energetically favorable sites by adsorbed atoms and thus to form a low-energy surface configuration is defined by the relation E0 ≏ 3kT, where k is the Boltzmann constant and T is the temperature. If the work function is above 0.13 eV, the energy of deposited particles is much more than 1 eV. In this case, radiation factor contributes to free energy of formed surface. It is particularly important to take this into account for deposition of two-component materials, such as transition metal carbides. In this case, heavy metal atoms deposition is accompanied by bombardment with light carbon atoms. For tungsten carbide with fcc lattice, this results in the fact that the flux density of primary particles (1 - 1.2)1016 cm-2 s-1, formation of [100] texture becomes
energetically preferably and provides the least damage ability of NaCl-type crystal lattice. In addition, light carbon atoms get the possibility to create grain boundaries and nanostructures for the occurrence in carbon sublattice of tungsten carbide. Increasing temperature under condensation up to 450 - 500°C results in decreasing critical particle flux density to 7 \times 10^{11} \text{ cm}^{-2} \text{s}^{-1}. At depressurization temperatures higher 500°C, intensive carbon desorption from the surface changes substantially element composition of growing coating. It was found that vacuum presence in carbon sublattice causes decreased ratio of elastic modules \( E_{[100]} / E_{[111]} \). Such variation is probably characteristic for all transition carbides, but especially it reveals itself in carbides with strong binding Me-Me (TiC, Mo-C, WC). For explanation of experimental effects, calculation models are proposed.

SESSION 04: MULTILAYERS, THIN FILMS

Chair: Ray Clark and Jeffrey M. Rickman
Wednesday by Morning, April 18, 2011
Salon 7 (Meeting Room)

8:30 AM #04.1

ATOMIC SCALE STRUCTURE OF GIANT MAGNETORESISTIVE MULTILAYERS. H.N.G. Wedley, X.W. Zhou, R.A. Johnson, Dept. of MS&E, University of Virginia, Charlottesville, VA.

The emergence of metal multilayers that exhibit giant magnetoresistance (GMR) to new magnetic field sensors, and new approaches for making nonvolatile random access memories. Controlling the atomic scale structure across the interfaces of these multilayers significantly improves the properties of these devices. However, the inability to manipulate atomic arrangements in this scale requires an understanding of the mechanisms that control hetero metal film growth during vapor deposition. It is important to both measure the position and identity of atoms at the atomic scale, and develop theoretical methods to assess the effects of deposition conditions upon this structure. Atomic simulation approaches have been developed to achieve this, and have been applied to analyze the atomic structure and GMR of sputter deposited CoFe/CoFe and CoFe/MoFe giant magnetoresistive multilayers used for magnetic field sensing. Significant improvement is seen in the CoFe on Cu interface, but not at the Cu on CoFe interface. The use of processing conditions that inhibit thermal fluctuations and atomic diffusion with impact energy control of the metal atom flux provides an effective means for control of the structure. A novel deposition process for the achievement of this control has been designed and found to produce superior films.

9:00 AM #04.2


We have sputtered Co/NiO bilayers on MgO (001) and (110) substrates. Epitaxial growth of NiO/MgO was evidenced by RHEED, X-ray diffraction, and spin-polarized STM experiments. First NiO (100) bilayers were obtained on MgO (001) with squares-on-square epitaxy. The Co grows in its fcc structure when deposited on NiO(001) at room temperature with the relative orientation Co[001][001]/NiO[0001][110]. This microstructure yields a four-fold in-plane anisotropy with the Co magnetic easy axes aligned along the NiO [110] directions. When the bilayer is annealed up to 300°C, the anisotropy switches to the [110] and [110] directions, the Co remaining epitaxial. The Co layers, deposited at 300°C and field-cooled to room temperature exhibit ahcp crystal structure with the c-axis aligned in the plane along either the NiO [110] or [001] direction. This indicates the appearance of two Co domains having their c-axes perpendicular. The resulting magnetic easy axes are aligned along the NiO [110] directions. For NiO deposited on MgO (110), we observe a self-organized nanostructure growth by HRTEM, RHEED and AFM. To minimize its surface energy, the Ni(110) grows with [001] and [010] facets whose width varies with the deposition temperature from 7 to 14 nm. These facets are elongated along the [001] NiO direction and can reach several micrometers long. The Co layers grow in the fcc structure conformally on these facets. Such a morphology results from a strong in-plane uniaxial anisotropy along [001] and an exchange bias along the same direction. Our results emphasize the role played by the crystalline structure and the morphology of the layers on exchange bias.

9:15 AM #04.3

THE EFFECT OF SURFACANTS ON THE GROWTH OF SPUTTERED Co/Cu MULTILAYERS. Branam L. Peterson, Bruce M. Clemens, Robert L. White, Stanford University, Department of MS&E, Stanford, CA.

In the growth of metal films on metal substrates, surface structure and kinetics play a very important role. By modifying the growing surface with an additional material (a surfactant), the growth mode and resultant film properties can be altered. In magnetic multilayers, the final properties are particularly sensitive to the film morphology and growth process. Cobalt/copper multilayers thus present an useful and relevant test case for surfactant assisted growth, with good lattice matching, but very different properties for all transition carbides, but especially it reveals itself in carbides with strong binding. Me-Me (TiC, Mo-C, WC). For explanation of experimental effects, calculation models are proposed.

9:30 AM #04.4

GROWTH AND STRUCTURE OF ULTRA-THIN X-RAY MULTILAYER STRUCTURES PREPARED BY MAGNETRON SPUTTERING. David L. W., Columbia University, Columbia Astrophysics Laboratory, New York, NY.

I will describe research directed at the development of multilayer structures prepared by dc magnetron sputtering, to be used as x-ray reflective coatings for X-ray astronomy. These thin film structures require smooth and sharp interfaces between polycrystalline and/or amorphous layers of optically dissimilar metals, alloys, insulators and semiconductors. Typical structures may contain as many as 1000 layers or more, with individual layer thicknesses ranging from less than 1 nm to several tens of nm. The achievable level of interface perfection is crucial for optimal performance interface imperfections (e.g., interface roughness and/or diffusion) typically must be less than 0.3 nm. I will present recent results from both experiments and atomistic computer simulations of thin film growth that illustrate the critical role of a variety of sputtering deposition conditions (e.g., background pressure, source collimation, sputter gas pressure, etc.) on film microstructure, interface morphology and stress, and demonstrate how such deposition parameters can be controlled in order to maximize performance.

10:30 AM #04.5

MODEL FOR INTRINSIC STRESS DURING THE EARLY STAGE OF POLYCRYSTALLINE FILM GROWTH. R.C. Cramnam, T.M. Trimble, Johns Hopkins University, Dept. of Materials Science and Engineering, Baltimore, MD; D.J. Schotvitz, Princeton University, Princeton Nanoscale Institute, Princeton, NJ.

A simple model for intrinsic stress generation in polycrystalline films resulting from effects of surface stress will be presented. This model can explain the development of compressive intrinsic stress often observed during the early stage of island growth. A physical picture for the generation of this stress is based on two effects. First, surface stress acting on an unconstrained island induce an equilibrium lattice spacing different from that of the bulk solid. Second, there a critical size where the island stress becomes flame anchored to the substrate. As a result of this later effect, an island larger than the critical size is no longer able to change its in-plane lattice spacing during further growth. Since the equilibrium lattice spacing will increase as the island grows, the island must impose a traction to keep the island from attaining the equilibrium spacing. If a post-critical island has a smaller in-plane lattice spacing relative to bulk, corresponding to a positive surface stress, this traction will result in a compressive intrinsic stress. A simple, linear elastic analysis of the mechanism incorporating the thermodynamics of surface stress will be presented. It will also be discussed how this mechanism may contribute to a sudden change in the intrinsic stress during island coalescence and ascompressive intrinsic stresses observed in certain fully grown polycrystalline films.

11:00 AM #04.6

THE DYNAMIC COMPETITION BETWEEN STRESS GENERATION AND RELAXATION MECHANISMS DURING VOLMER-WEBER FILM GROWTH. J.A. Poole and S.J. Henne,
Substrates and Epitaxial Islands.

Anamalai Lakshminarayana, Vidya Yegn, Alex King, Eric Kwen, Purdue University, School of Materials Engineering, West Lafayette, IN.

A model to account for misfit dislocation array image effects during epitaxial island growth is presented. Misfit dislocations often appear at an interface between phases to accommodate a lattice mismatch. In many situations, such as early film growth, one of the phases may be discontinuous, leaving the interface region clearly bounded. The structure of such a finite interface differs from the normally-modeled infinite interface because of end effects near the boundary. We have modeled the dislocation structure of such a finite interface, MBE-grown InAs on GaP, and compared our results to high resolution images of the same structure. The 1.1% misfit causes dislocation introduction of growth. Islands containing from 4 to 14 dislocations were examined, and dislocation spacings were found to be larger approaching the perimeter. Our calculations, which considered the image forces associated with the misfit dislocation array, model the observed structures well.

SESSION 05: EARLY STAGES OF FILM GROWTH

MECHANICAL PROPERTIES

Chairs: Steven M. George and Robert C. Cimmaron

Wednesday, Afternoon, April 18, 2001

Salon 7 (Marriott)

1:30 PM *05.1 IMPACT OF NUCLEATION CONDITIONS ON TRANSFORMATION KINETICS AND MICROSTRUCTURE IN THIN FILM SYSTEMS. J. M. Redman, Dept. of MSE, Lehigh University, Bethlehem, PA.

We examine quantitatively the impact of various nucleation conditions on the temporal evolution of a phase transformation, with particular emphasis on thin-film systems. Specifically, we characterize transformation kinetics and associated microstructures for a polycrystalline nucleation on crystalline defects and for cases in which there is a short-range interaction between nuclei. This is accomplished via the calculation of non-equilibrium, n-point correlation functions as well as related descriptors of spatial point processes using both computer simulation and complementary analytical work. One goal of this work is to relate both kinetics and microstructure to the underlying properties of the generating point process. Finally, in order to connect our models to experiment, we also discuss image-processing strategies that have been employed to interpret relevant TEM micrographs.

2:00 PM *05.2 CORRELATIONS BETWEEN ISLAND NUCLEATION AND GRAIN GROWTH FOR POLYCRYSTALLINE FILMS. C. Eisenmenger-Stichter, A. Bergner, Institut für Angewandte und Technische Physik, Technische Universität Wien, Vienna, AUSTRIA.

For Physical Vapor Deposition (PVD) processes the nucleation and growth of stable islands on monocrystalline and even polycrystalline substrates can be described by the rate equation theory in a mean field approximation. The observable quantity which can be derived from the rate equations is the global density of stable islands. Individual correlations and island size distribution on the other hand, cannot be obtained from this formalism. The array of stable islands, in turn, forms the template for the subsequent growth of a polycrystalline thin film. For the initial grain shape and grain size therefore both, the global island density as well as possible inter-island correlations play a key role. This paper presents the results of simulations which take into account the effects of both, the global island density as well as island/island correlations on the growth of a thick polycrystalline film. The simulations consist of two steps: first a polycrystalline template is generated from an initial distribution of stable islands by employing an algorithm for the construction of Voronoi zones. The Voronoi zone network mimics the state of the film just after island coalescence and just before the onset of grain growth. Then the well known q-state Potts model of grain growth is employed to study the further steps of microstructural evolution. A higher initial island density leads to broader islands while a very homogeneous distribution of islands significantly retards grain growth. The reasons for these effects are briefly discussed.

2:15 PM *05.3 MAGIC NANOSTRUCTURES DURING THE EARLY STAGE OF THIN FILM GROWTH. M. Zhang, M. Yu, Efremov, F. Schiettekatte, E.A. Olson, A.T. Kwan, J.T. Warren, R.S. Berry, J.E. Greene, and L.H. Allen, Dept. of Materials Science and Engineering and Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL.

The behavior of thin indium films at their early growth stage is
in-situ investigated by a novel ultrasonic thin film scanning calorimetry technique. These films consist of ensembles of island nanostructures on the melting surface of the melt. As the heat of fusion is strongly influenced by their dimensions, we experimentally determine the relationship between the nanostructure radius and the melting point as well as the size effect on the latent heat of fusion by combining the atomic resolution and laser manipulation of nanostructures with a size distribution obtained from Transmission Electron Microscopy studies. A linear melting point depression phenomenon is observed. Moreover, by looking at the fine structures of these caloric curves, we observe new phase transitions in high-temperature superconductors. The melting enthalpy, capacity, and volume of the nanoscale heat capacity samples show several local maxima at certain temperatures. This suggests that preferred energy states exist among these self-assembled island nanostructures on the amorphous surface during the early stages of thin film growth. These maxima correspond to each other according to the nanostructure sizes by introducing one monolayer of indium atoms in thickness, which could be extended to other materials observed previously in free-standing films. (1) M.Y. Efremov, F. Schietekate, M. Zhang, E.A. Olson, A.T. Kuan, R.S. Berry and L.H. Allen: "Direct atomic scale melting point observations for nanostructure ensembles". Phys. Rev. Lett. 85, 3560 (2000) (2) M. Zhang, M.Y. Efremov, F. Schietekate, E.A. Olson, A.T. Kuan, L. S. Lai, J.E. Greene and L.H. Allen: "Size-dependent melting point depression of nanostructures: Nanometric measurements" Phys. Rev. B., 62, 10568 (2000)

2:30 PM 05.4 NUCLEATION PHENOMENA AND MICROSTRUCTURE EVOLUTION OF VAN DER WAALS EPITAXY FILMS
E. Wieckowski, W. Jagermayer, Materials Science Department, Darmstadt University of Technology, Darmstadt, GERMANY.

(Quasi) Van der Waals epitaxy allows the epitaxial growth of lattice-mismatched heterostructures. However, high-quality films can only be expected when detrimental grain boundaries between different surface grains can be avoided. We have systematically investigated the growth of metals and 2D semiconductors on layered chalcogenide substrates with a systematic variation of substrate temperature and flux rates. The initial nucleation and subsequent film growth was studied by a combination of photoemission (XPS, UPS), electron diffraction (LEED) and scanning probe techniques (UHV-APM/STM). The results show that different orientations of nucleation clusters are formed. Only some of them may intergrow to layer crystallites whereas others form grain boundaries at their contact area. The implications of these results for the perspective of (Quasi) Van der Waals epitaxy for preparing interfacial buffer layers will be discussed.

3:15 PM 06.5 DYNAMICS OF ELASTIC BUCKLING INSTABILITY
Leonid Golobovik, West Virginia University, Department of Physics, Morgantown, WV.

Although buckling instability of compressed thin objects is a classical subject, little is known on dynamical aspects that go with buckling phenomena. First deeper insights into buckling dynamics will be reviewed in this talk on the buckling dynamics of strained objects such as thin films and thin sheets (solid membranes). In recent investigations using nanometer-scale measurements, we observed the very fundamental nature of the dynamics of buckling phenomena in strained thin sheets and flexible rods. We related their buckling dynamics to that of the phase ordering phenomena such as the formation of ordered domains in magnetic systems below critical temperature \( T < T_c \). Evolving this sheets develop morphologies similar to that of growing interfaces, characterized by the presence of mounds with a size that grows as a power of time. Membrane morphology is characterized by the presence of a network of growing ridges where the elastic energy is mostly localized. We used this fact to develop a scaling theory of the buckling dynamics and deduce the coarsening exponents. Our findings have shown that the buckling dynamics constitutes a new class of coarsening phenomena for which characterized by spectral scaling not found before in magnetic systems or elsewhere. [1] L. Golobovic, D. Molkov, A. Perepocha, Phys. Rev. Lett. 81, 3387 (1998). [2] D. Molkov and L. Golobovic, Phys. Rev. Lett. 82, 2884 (1998). [3] D. Molkov and L. Golobovic, Phys. Rev. E60, 4577 (1999). [4] L. Golobovic, D. Molkov and A. Perepocha, Phys. Rev. E61, 1783 (2000).

4:45 PM 05.6 ELECTRON-Beam-DIRECTED VAPOR DEPOSITION OF MULTIFUNCTIONAL STRUCTURES
Douglas T. Queheillalt, Yash Kasum and Hyun N.G. Wedley, Department of MSE, School of Engineering and Applied Science, University of Virginia, Charlottesville, VA.

Multifunctional structures are those which combine load bearing support in addition to supplemental functions such as actuation, electrochemical energy storage or thermal management. Electron Beam-Directed Vapor Deposition (EB-DVD) technology has been used for the deposition of templated cellular structures and porous electrode coatings for rechargeable metal-air and -metal hydride cells. In addition to load bearing support, the templated cellular structures exhibit enhanced thermal management characteristics and the electrochemical cells can be integrated into the load bearing supports of the flexible and mobile structures leading to their multifunctionality. During EB-DVD, the electron beam evaporated vapor flux is encompassed by a rarefied transonic inert gas jet, entraining the vapor in a non-reactive gas flow and transporting it onto the collector portion of the electron beam. High EB-DVD technology has been used to synthesize Al and Zr based templated cellular structures for thermal management systems and porous nickel coatings for the positive electrode and porous rare earth (misch) metal electrodes based on La and Zn (AB2 alloys) for the negative electrode of rechargeable nickel - metal hydride cells.

4:00 PM 05.7

4:15 PM 05.8 NANOINDENTATION AND MICROSTRUCTURAL EVOLUTION STUDIES OF DC MAGNETRON SPARKED CHROMIUM NITRIDE THIN FILMS
Ankur B. Agrawal, B.A. Rainey, S.M. Yulaev and J.C. Bilelo, Center for NанoMaterials Science, Department of MSE, University of Michigan, Ann Arbor, MI. "Now at Advanced Micro Devices, Sunnyvale, CA. "Now at IBM, Burlington, VT.

Nanoindentation experiments have been performed to assess the mechanical behavior of chromium nitride (CrN\(_2\)) thin films sputtered in different deposition geometries and with varying Ar and N\(_2\) pressures. The hardness and elastic modulus of chromium nitrides are of great interest with regard to their applications. In the present work, two different deposition geometries, i.e., multi-substrate and confocal, were used to sputter (DC magnetron) a CrN\(_2\) layer on Si (100) wafers at varying nitrogen flow rates. The results of the nanoindentation experiments indicate that, over a similar region and nitrogen regime, the CrN\(_2\) films grown in a multi-substrate geometry exhibit higher hardness and elastic modulus on the wafer than those grown in the confocal geometry. Furthermore, it was found that in the multi-substrate geometry the hardness and elastic modulus of these films were significantly higher than those in the confocally deposited films for a specific regime of the nitrogen flow rate (10-14 sccm).

Finally, observations of the mechanical properties trends could be correlated with a higher degree of anisotropic structures grown in the multi-substrate in comparison to the confocal geometry.

4:30 PM 05.9 FRICTION AND WEAR BEHAVIOR OF Al-Cu-Fe-B QUASICRYSTALS
Xiyong Zhou, Dept. of Materials and Science, Nanchang Institute of Astronautical and Technology, Nanchang, CHINA; Carolin Riched, Dept. of Materials, Univ of Technology of Compiegne, Compiegne, FRANCE.

Dry sliding wear between the polycrystalline AlCuFeB 25.5GPa 12.5B3 quasicrystals and coating of the Diamond-like Carbon (DLC) is carried out by selfmade tribometer under different conditions. The influences of four parameters (temperature, sliding speed, applied load, the atmosphere) on friction and wear of quasicrystal surface are studied. In addition, the surface microscopy and the microstructure have been observed by scanning electron microscopy (SEM) and X-ray diffraction. The results show that, with rise of the applied load and sliding speed, the friction coefficient decreases. The friction coefficient is increased greatly by the presence of water. The wear mechanism illustrates that not only abrasive wear but also adhesive wear exist in surface of the quasicrystals. At 350°C, the wear mechanism is mainly wear mechanism for quasicrystal. Moreover, Anisotropy of the surface morphology illustrates that the microcrack [or sub-crack] form to different extent, in all worn quasicrystal surface. All discussion and analyses of the results on experiment are presented in detail. Keywords: Quasicrystal, Temperature, Friction coefficient, Microcrack

SESSION 6: TEXTURE IN POLYCRYSTALLINE FILMS
Chair: Leonid Golobovik and David L. Wind
Thursday, March 19, 2009.
Salon 7 (Marriott)

8:30 AM 06.1 MATHEMATICAL MODELS OF ION BEAM ASSISTED DEPOSITION OF MgO
Peter Smerick, Dept. of Mathematics, University of Michigan, Ann Arbor, MI.
One of the promising approaches to producing superconducting tape using YBCO on the YIGO substrate. Typically, a MgO substrate will be polycrystalline film with a (100) fiber texture. However, to obtain a high quality superconducting tape it has been determined that one needs MgO films with good in-plane texture. One of the approaches to this problem is to use the in-plane texture using narrow band level set methods. Computations of IBAD MgO will then be presented. We still need to explore various models of IBAD MgO and the level set approach is, unfortunately, too slow to compute. The models of IBAD MgO growth with a large number of crystals. For this reason, a simplified computational strategy has been developed which allows for the approximate solution of the mathematical model for IBAD MgO. The results of the simplified approach are not yet available in the literature. The key parameters that control the in-plane texture are the seed nucleation density and the out-of-plane texture. The model shows that there is no optimal film thickness, after which the in-plane texture will not improve and the surface roughness increases. Furthermore, the MgO surface appears to tilt toward the ion beam. The predictions of the in-plane texture are in reasonable agreement with experimental results as the threshold film thickness. (This is joint work with G. Russo, X. Li, and D. Smokier)

9:00 AM O6.2

IN SITU 3D AXIAL TEXTURE ANALYSIS OF MgO FILMS GROWN DURING GROWTH ON AMORPHOUS SUBSTRATES BY ION BEAM-ASSISTED DEPOSITION. Rheti T. Brewer1, Paul N. Arendt2, James R. Groves3, and Harry A. Atwater4. California Institute of Technology, Tech of Applied Physics, Pasadena, CA. Los Alamos National Laboratories, Los Alamos, NM.

Ion beam-assisted deposition (IBAD) has been demonstrated to produce biaxially textured thick films on amorphous substrates. Magnesium Oxide is particularly interesting because its biaxial texture is optimally developed within the 1-11 nm of growth, and single crystal MgO has already been studied as a heteroeptactile template for ferroelectrics and superconductors. However, obtaining experimental evidence to examine the biaxial texturing mechanisms of IBAD MgO has been difficult due to the small size of the key parameters controlling the in-plane texture. We have extended the conventional axial texture analysis techniques and the difficulties associated with studying thin films of MgO with X-rays. We have used a previously reported RHEED based method for performing quantitative analysis of mosaic polycrystalline thin film in-plane and out-of-plane grain orientation distributions to examine in-situ axial texture measurements of IBAD MgO. RHEED in-plain rocking curve analysis of IBAD MgO films, at 25keV and 2.7° incidence angle, measures in-plane orientation distributions on the order of 4° to 5° narrower than measured using X-ray rocking curve analysis or transmission electron microscopy (TEM). Because biaxial texture typically improves as film thickness decreases, we have used RHEED to examine the in-plane orientation distributions of films of varying thickness. These measurements indicate that RHEED in-plain rocking curves offer surface sensitivity that X-ray diffraction for analyzing film in-plane orientation distributions. RHEED is sensitive to films as thin as 30 nm. However, this sensitivity requires us to sequentially observe the biaxial texture from just after grain nucleation, through island growth, film coalescence, and complete coverage. The degree of biaxial texturing accomplished during nucleation and the rate of biaxial texture evolution during film growth have been examined (when ion-induced anisotropic sputtering is most important), as well as film coalescence (when both ion-induced anisotropic grain damage and sputtering can improve biaxial texture) will be discussed.

9:15 AM O6.3

PHASE FIELD SIMULATIONS OF OBLIQUE INCIDENCE BALLISTIC DEPOSITION. Myrkan Brancher1, James P. Sethna2, Cornell University, Dept. of Physics, Ithaca, NY. Iago Wang3, Washington University, Dept. of Chemical Engineering, Ithaca, NY.

Recent developments in energetic beam deposition techniques allow to deposit metals and semiconductors on surfaces with controlled energy and incident angle. For oblique incidence, formation of columnar structures has been observed experimentally as well as in Kinetic Monte Carlo (KMC) simulations. We study the growth of these structures in a continuum phase field model, to overcome the limitations of KMC. Our model includes shadowing, anisotropic surface tension, and angle dependent sticking rates. We study the growth angle and coarsening behavior as a function of the incident angle and compare our simulations results with experiments and KMC simulations.

9:30 AM O6.4

HIGH-FLUX LOW-ENERGY ION BOMBARDMENT ENHANCED CRYSTALLINITY OF POLYCRYSTALLINE Si THIN FILMS. Jennifer E. Gerbi1, John R. Abeles2, University of Illinois at Urbana-Champaign and Coordinated Science Laboratory, Urbana, IL.

We deposit polycrystalline silicon films at low temperatures (400°C) on glass using magnetron sputtering at low pressures. Using an external magnetic field, we balance the magnetron, increasing the ion/nuclear flux ratio while reducing the ion energy via substrate bias to ~20eV; this energy is large enough to promote adatom evaporation but is too small to produce sub-surface point defects. Using Raman scattering, ellipsometry, TEM, and AFM, we show that this shower of low-energy, high flux ions on a Si substrate (50 keV) from 40nm to 100nm thick films) while keeping the films extremely smooth (1.9nm rms surface roughness). The thickness of the interface layer of amorphous silicon that exists before the polycrystalline Si nucleates is also strongly diminished, indicating that nucleation barriers are reduced. The mechanism by which the ions enhance crystalline growth is studied here by performing two experiments using in-situ, full spectroscopic, fast ellipsometry. Ion-enhanced epitaxy experiments are performed on Si substrates to probe the epitaxial thickness and quality as a function of arriving ion flux and energy. Additionally, growth is performed on intentionally rough substrates, and the rate of smoothing is measured as a function of ion flux. We interpret both results in terms of ion bombardment enhanced adatom diffusion, and discuss the mechanistic implications for direct deposition of polycrystalline Si at low temperatures.

9:45 AM O6.5


The sputter deposition of Al and Cu onto a foreign substrate usually results in 3D island nucleation, eventually, coalesced, and eventually, coalesced, to form a polycrystalline film. The relatively high diffusivity of these materials permits the transport of deposited material across the substrate, and transfer between islands, so as to reduce the total surface, interfacial and bulk strain free energy. The Al and Cu films used in Si device metallization are examples of this process, since the Al conductor layers are usually deposited by sputtering, as well as the Cu seed layer. There are problems with the formation of voids in Al films during deposition, primarily as the islands coalesce, and with the incomplete coverage of the barrier layer films of the Cu seed layer. Voids can act as preferred sites for electromigration, and for de-wetting of the film from the substrate during annealing. We have developed Monte Carlo simulations to study island growth and coalescence during deposition, and to predict the resulting microstructure of the films, including voids and grain boundaries. These simulations give the thickness of which island merger occurs, and thus the minimum thickness required for the formation of a continuous film. We have developed a novel model of island growth in order to provide fast estimates of coverage and film quality, using Monte Carlo simulations only to test the applicability of the analytical model to different conditions of film growth. We have also applied the Monte Carlo simulations to study the influence of various deposition techniques on the structure of the films. We have examined the influence of energetic beams on the nucleation and merger of clusters, as well as that of substrate bias. Results of these simulations are validated using sputter deposition experiments, including magnetron sputtering systems similar to those used in the fabrication of Si devices.

10:30 AM O6.6

MULTISCALE MODELLING OF GROWTH OF POLYCRYSTALLINE THIN FILMS. James B. Adams1, Jie Zheng2, Zhiyong Wang3, Arizona State University, Dept. of Chemical and Materials Engineering, Tempe, AZ.

We have developed two new modeling tools for studying the growth of polycrystalline thin films. POLYFOW and FACET-POLYGROW is a 3D polycrystalline kinetic lattice Monte Carlo code that can simulate the deposition of BCC metals for long times. It is based on the lattice diffusion model of the atom-scale and mesoscopic aspects of film growth. We will present results for the deposition of Mo films, the effect of chemical etching, and the effect of long-term annealing on the tip structure. FACET is a 3D simulation of polycrystalline film growth on the micron scale. It models films in terms of individual grains, with each grain having its own orientation, surface facets, and grain boundaries. It includes both deposition and surface diffusion events, with surface diffusion rates calculated by a 3D and for 1D kinetic Monte Carlo model. This code allows one to model the evolution of grain morphology during film growth in real time. We will present several results relevant to PV of Cu.

11:00 AM O6.7

CORRELATION BETWEEN SURFACE AND MICROSTRUCTURE EVOLUTION IN MBE DEPOSITED AI FILMS ON Si (111) AND
An investigation of the microstructural evolution of Al(Cu) thin films deposited on a variety of interlaved dielectric (ILD) layers was performed. A combination of X-ray textural measurements and scanning electron microscopy (SEM) was employed to link the texture behavior of the Al(Cu) films as deposited on ILD layers at thicknesses to the observed morphological development within the films. Three regimes of texture were observed, corresponding to (1) Al(Cu) island growth and individual island coalescence, (2) fully coalesced film and the onset of grain growth and (3): extensive grain growth. The first and last of these regimes exhibited offset [111] texture, in which the maximum diffraction intensity from Al(111) is offset from the substrate normal. However, the behavior of maximum offset texture differed between the two stages of growth, indicating that the two different mechanisms were responsible. The offset [111] texture observed in the third regime of Al(Cu) film microstructure was due to the faceting of grain surfaces. The time required for the film to reach these stages depended on the interaction of the Al(Cu) adatoms on the ILD surfaces, which differed in chemistry and topology. Because research on Al(Cu)/Ti/ILD structures revealed a dependence of the offset [111] texture on ILD morphology, a link between the remnants of island growth in the Al(Cu) films directly onto ILD’s and their subsequent grain orientations during the final growth stage will be discussed.


1:30 PM 07.1 SURFACE BOUNDARY AND TRIPLE JUNCTION EFFECTS DURING GRAIN GROWTH IN POLYCRYSTALLINE FILMS

Amrinda L. German, Dept of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL

Elizabeth A. Holm, Materials Theory and Computation, Sandia National Laboratories, Albuquerque, NM

Alexander H. King, Rachel F. Cefalu, School of Materials Science and Engineering, Purdue University, West Lafayette, IN

Grain growth in polycrystalline films commonly ceases when the mean grain diameter is approximately equal to the film thickness. Theoretical Monte Carlo grain growth simulations were used to explore three proposed mechanisms for this stagnation: grain boundary growth, triple junction drag, and low triple junction free energy. When surface boundaries have a lower mobility than bulk boundaries due to grain boundary grooving, grain growth slows but does not stop, nor do the crenoidal grains, abnormal triple junction angles, or typical grain size distributions predicted by theory occur. If reduced triple junction mobility causes triple junction drag, grain vertex angles deviate from 120 degrees and the grain size distribution narrows, but the total curvature per grain boundary, thus the driving force for growth, remains constant. Therefore, while growth kinetics decrease, stagnation again does not occur. When triple junctions have a negative free energy relative to grain boundaries [as proposed by King (1)] three regimes are observed. For the lowest triple junction energies, the system disorders. For high triple junction energies, normal growth occurs. For moderate triple junction energies, three-dimensional systems disorder, but columnar (two-dimensional) polycrystals grow normally. In no case is stagnation observed. These results are compared to experimental observations using a new method for measuring boundary mobility for grain growth. Grain boundary migration is a fundamental process governing grain growth. The motion of a grain boundary is significantly affected by the presence of a free surface because of the formation of a groove at the triple junction. The interaction of grain boundary migration and thermal grooving has not been studied in detail. We have coupled thermal grooving and grain-boundary migration for inclined grain boundaries, and obtained free-surface and grain-boundary profiles. We assume that thermal grooving results from surface diffusion whereas grain boundary migration obeys a curvature-driven law of motion. A range of length and time scales are needed to...
describe the coupled motion. It is found that the grain boundary is never pinned. We will present these results and discuss the implications.

2:00 PM 07.3
ROLE OF SUBSTRATE AND GROWTH PROCESSES ON TEXTURE EVOLUTION IN VAPOR DEPOSITED AI AND Cu THIN FILMS. John Sanchez Jr., Advanced Micro Devices, Sunnyvale, CA; Adriana I. Ten, Lucent Technologies, Reading, PA.

Successful strategies for controlling the microstructure of vapor deposited thin films include proper choice of substrate or barrier materials. However, understanding of the various mechanisms responsible for microstructure control by the substrate is incomplete. We present the characterization of spatter deposited 6 Al and Cu thin films from 10 nm to greater than 1000 nm in thickness on SiO2, Ti and Ta layers by x-ray pole figures, atomic force microscopy and cross-section transmission electron microscopy. The 10 nm thick Al films on SiO2 and Cu 10 nm films are crystallized and oriented. However, the 10 nm Al on SiO2 is discontinuous and consists of both faceted and rounded islands. We show that the faceted islands are larger than average size and are oriented 5 degrees from exact fiber orientation, whereas the rounded islands are randomly oriented. Upon achieving film continuity these larger/faceted/5 degree tilted Al grains promote the evolution of the near (111) 5 degree film texture characteristic of Al films on SiO2. In contrast the 10 nm Al on Ti is continuous, and an exact Al (111) fiber texture emerges as a result of normal and abnormal grain growth concurrent with continued deposition. Similarly, the texture of 10 nm thick Cu films is also primarily randomly oriented, with the exact Cu (111) fiber texture evolving as grain growth and deposition proceed. We conclude by discussing the combination of islands stage growth mechanisms, abnormal and normal grain growth processes and substrate effects as microstructure develops during deposition.

2:15 PM 07.4

Texture evolution in polycrystalline thin films is a direct result of processes occurring both during the nucleation stage of film growth, and during recrystallization or grain growth in continuous films. We will present preliminary measurements of texture evolution in Ag and Al thin films using a new in situ x-ray diffraction capability. In this talk we will discuss the real-time evolution of (111) and (100) fiber textures during annealing of Ag and Al films, and correlate texture evolution with grain growth. When Ag is deposited at temperatures in the range 50 to 80°C, and then warmed to room temperature and above, texture development exhibits a sharp onset near 100°C, for films with thicknesses that vary by an order of magnitude. By contrast, Al films deposited under similar conditions exhibit a continuous deposition of texture with temperature. For Ag films, a competition between (111) and (100) textures is observed, with the preference for (111) increasing with increasing film thickness. Only (111) texture is observed in Al films. The x-ray data also contains information on the nearness of the (111) texture to the (111) orientation with temperature for both the (111) and (200) texture components. These results will be interpreted within a framework of orientation-specific grain growth that minimizes both surface and elastic energy. The film/multiatomic layer memory optical device. Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC03-76-SF00098.

2:30 PM 07.5
MICROSTRUCTURAL COMPARISON OF Ag FILMS GROWN ON AMORPHOUS TiO2 AND POLYCRYSTALLINE ZnO. Randi Duerrstark, Darin Glenn, AFG Development Corporation, Santa Clara, CA; Tony S. Yoon, National Center for Electron Microscopy, Lawrence Berkeley Lab, Berkeley, CA.

16 nm Ag films were sputter deposited onto amorphous TiO2 underlayers 25 nm thick, and also amorphous TiO2 (25 nm) ZnO (5 nm) multilayered films. The substrates were back-sputtered Si with a 50 nm thick LPCVD Si3N4 electron transparent membrane. The ZnO, sputtered onto amorphous TiO2, formed a continuous layer with a grain size of 5 nm in diameter, on the order of the film thickness. There are several microstructural differences in the Ag dependent on the underlayers, revealed by TEM. First, on TiO2 the Ag microstructure shows many abnormal grains whose average diameter is about 50 nm, whereas on ZnO several abnormal grains are present. The background matrix of normal grains on the TiO2 is roughly 15 nm, while the normal grain size on the ZnO is about 25 nm. Electron diffraction patterns show that the film on ZnO has a strong (111) and (200) peak and dark field images with this diffraction condition have a grain size of about 30 nm. In a region near the center of the TEM grid where there is the greatest local heating during deposition, Ag films grown on amorphous TiO2 are discontinuous, whereas on ZnO, the film is continuous. When films are grown on solid glass substrates, with ZnO underlayers have sheet resistances of 5.68 ohm, whereas those on TiO2 are 7.56 ohm. The conductivity difference is very repeatable. The improved conductivity is thought to be the combined effect of reduced grain boundary volume, the predominance of low grain boundary residual concentration Coincidence Site Lattice boundaries from the (111) orientation, and Ag plating on ZnO resulting in less groove formation on deposition.

2:45 PM 07.6
INFLUENCE OF THE SPATTERING GAS ON THE PREPARED ORIENTATION OF NANOCRYSTALLINE TITANUM NITRIDE. Thai Le, Gregory Thoren, University of Maine, Orono, ME; James L. Frasier, Dept. of MSCE, Ohio State University, Columbus, OH; Ramesh Chandra, Dept. of Physics, Guru Nanak Dev University, Amritsar, INDIA; Pusham Ayub, Dept. of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai, INDIA.

Titanium nitride thin films have a wide variety of applications both for structural as well as electronic applications. Their hardness makes them ideal candidates for wear resistant applications. In addition, the excellent electrical conductivity of titanium nitride combined with the fact that it is a good diffusion barrier makes it an excellent contact material in the microelectronics industry. Nanocrystalline titanium nitride thin films have been deposited by high pressure reactive magnetron sputtering from an elemental titanium target using a mixture of an inert gas and nitrogen. The mean crystallite or grain size in these films is in the range 5-12 nm measured from the Debye-Scherrer line broadening in the x-ray diffraction pattern. Interestingly, the type of inert gas used in the sputtering gas mixture significantly influences the preferred orientation of growth in these films. Thus, using a helium and nitrogen gas mixture results in a strongly (002) oriented film whereas using a neon and nitrogen gas mixture results in a strongly (111) oriented film. In addition, films have also been deposited using pure nitrogen as the sputtering gas. The films deposited using pure nitrogen exhibited a strong (002) orientation and had a significantly larger grain size as compared with those deposited using a mixture of an inert gas and nitrogen. Details of the microstructural evolution in these films based on x-ray characterization using transmission electron microscopy will be discussed in this paper. The ability to tailor the size of crystals and their preferred orientation in these films is expected to have a significant impact on their properties for a variety of technological applications.

3:30 PM 07.7

Tungsten atomic layer deposition (ALD) can be accomplished by repeating the binary reaction WCl6 + SiH4 → W + 2SiH3Cl + 2H2 in two self-limiting half-reactions. Successive exposure to WCl6 and SiH4 in an ALD apparatus has produced W ALD at a rate of 2.4 A per ALD cycle at 425 K. The nucleation and growth during W ALD on oxide surfaces have been using Auger electron spectroscopy (AES). The AES results displayed an initial nucleation period of 7-8 A, and then deposition one tungsten monolayer on SO4. The W and Si AES signals grew and oscillated dramatically versus WCl6 and SiH4 exposures. An examination of the oxygen and tungsten AES signals versus AB cycles indicated that W ALD deposited nearly ideal layers by layer. Frank van der Merwe growth after the nucleation period. The AES results displayed a shorter nucleation period of 3-4 AB cycles for W ALD on Al2O3. The W and Si AES signals grew oscillated versus WCl6 and SiH4 exposures. However, the oxygen and tungsten AES signals showed AB cycles on W ALD on Al2O3, the ALD cycle was not completely wet the underlying Al2O3 surface. The W ALD was consistent with Stranski-Krastanov or Volmer-Weber growth with tungsten coverage of 85% of the Al2O3 surface. The initial nucleation period for W ALD is important since these cycles per cycle required for nucleation can affect the roughness of the resulting ALD films.

4:00 PM 07.8
COMPARISON STUDY FOR TIN FILM DEPOSITED FROM DIFFERENT METHODS: CHEMICAL VAPOR DEPOSITION AND ATOMIC LAYER DEPOSITION. Byung Yung Kim, Sung Hye Lee, Ki Young Oh, and Juho Song, Jusang Engineering Limited, Kyung Ki Do, KOREA.

Recent advanced semiconductor devices require metal barrier processes of low process temperature and excellent film step coverage without the degradation of resistivity and impurity content level in
the film. This paper compared two different film deposition processes for formation of TiN barrier layers, conventional TiC-based chemical vapor deposition or atomic layer deposition (ALD). The TiC-based TiN films deposited by conventional TiC-based CVD at the process temperature of 600°C followed by NH3 post-deposition anneal showed about 180 µm of resistivity, over 95% of step coverage for the pattern aspect ratio of 1:1, 0.1 µm contact diameters, and below 2% of Cl content in the film. Meanwhile, the films deposited by ALD at 100°C lower process temperature than CVD even without post-deposition anneal showed much better film properties which were almost the same as the original values and better step coverage characteristics. More detailed material analysis was done by AFM, XPS, SEM, and AES. Studies of film growth processing parameters such as process temperature, reaction gas ratio, chamber pressure, post-deposition anneal for both methods and analysis results would be included.  

4:15 PM P 07.0  
Abstact Withdrawn.

4:30 PM P 07.10  
NANOSCALE TEXTURE DETERMINATION AND EVOLUTION IN ULTRA-TIN-TIN FILMS  
Mark J. Williamson, Derren Dunn, Robert Hall, University of Virginia, Department of MSE, Charlottesville, VA; Suneel Kodinakula, Ivan Petrov, Joe Greene, University of Illinois, Department of Materials Science, Urbana, IL.  
As the feature size of devices in integrated circuits continues to shrink there is a need to characterize polycrystalline materials on decreasing length scales. For example, it is necessary to develop ultra-thin diffusion barriers for interconnect structures, and a critical part of this development is to ensure that these barrier materials have the optimum grain structure and texture. We will present results on the texture evolution and grain morphology in fine-grained TiN thin films. In order to do this we have developed a technique using cross-correlation of dark-field images obtained using annular objective apertures in the transmission electron microscope, with annular radii that correspond to the low index TiN reflections. This technique enables parallel analysis of the orientations of thousands of grains, with a spatial resolution of order 10 nm. This combination of spatial resolution and high throughput is not possible with x-ray diffraction, electron backscattered diffraction or conventional transmission electron microscopy. Preferred grain orientations were determined for 48, 69, 80- and 150nm-thick TiN layers grown on amorphous SiO2 at 400°C by magnetron-sputtered reactive magnetron sputter deposition. We find that no single orientation is dominant in the 48 nm films but that a <100> texture develops and continues to grow by the time these films reach 60 nm thickness. These results demonstrate that in ultra-thin diffusion barriers, processing conditions will have to be carefully understood and designed to ensure optimum microstructures.  

4:45 PM P 07.11  
EFFECT OF RAPID-THERMAL-ANNEALING ON TiN FILMS AS THE BARRIER LAYER FOR THE Pt/BST/Pt CAPACITORS PREPARED BY RF MAGNETRON CO-SPUTTER TECHNIQUE AT LOW TEMPERATURE.  
Min-Hung Jung, National Taiwan University, Department of Electronic Engineering, Taipei, TAIWAN; Chia-chou Hwang, Huang-Chung Cheng, National Chiao-Tung University, Dept. of Electronics Eng., Hsin-chu, TAIWAN.  
This barium strontium titanate (BST) film with a high dielectric constant has attracted much attention for practical use in high-density DRAM capacitor. In the capacitors of capacitor-over-bistable oxide (COB) structure, a diffusion barrier of TiN is often used to prevent the electrode and dielectrics from chemical reaction with poly-Si plug and TiN adhesion layer during BST deposition and post-processes. In this study, the Pt/BST/Pt/TiN/Si structure is used to simulate the practical COB capacitor structure. Effect of rapid thermal annealing on metallic barrier TiN against the diffusion of Ti and Si into BST has been investigated. In the integration of BST capacitors, the thermal budget of the BST deposition would cause the interdiffusion of Ti and Si from Ti adhesion layer and poly-Si plug respectively. This event would degrade the BST capacitors. To address this issue, rapid-thermal-annealed TiN barrier was deposited between the bottom electrode Pt and the adhesion layer Ti. By RTA treating the barrier layer, good barrier properties were achieved. The RTA treatment at 600°C for 90 sec can improve the crystallinity of TiN and suppress the formation of unexpected materials. Excellent electrical characteristics of the Pt/BST/Pt/TiN/Si capacitors, including a high dielectric constant of 220, a low leakage current of 15 nA/cm² under a 1 volt bias and a lifetime longer than 10 years under 1.6 MV/cm were obtained for the BST films formed by using co-sputtering with an Ar O₂ mixed ambient at a low substrate temperature of 300°C. On the other hand, the TiN barrier was not suitable for excessively elevated RTA temperature above 700°C. Owing to such high roughness asperity of the Pt/TiN surface formed during the RTA treatment at 700°C, the leakage current increased significantly and dielectric degradation was thereby accelerated.  

SESSION 08: POSTER SESSION  
Chair: John E. Magee, University of Western Ontario, London, ON, Canada; George H. Gibner, Thursday Evening, April 10, 2001, 8:00 PM  
Salon 1-7 (Mezzochi)  

08.1  
MODELLING OF GALLIUM NITRIDE GROWTH FROM TRIMETHYL GALLIUM AND AMMONIA: REACTIONS PATHWAYS AND RATES.  
Debina Sengupta, Sindip Manna, CFD Research Corporation, Huntsville, AL.  
Reactor scale modeling of chemical vapor deposition has recently drawn much attention due to its potential for cost effective development of next generation solid-state devices. The most challenging aspect of the large-scale reactor modeling is the accurate determination of the rate constants of reactions occurring between the precursors, both in the gas phase and at the surfaces. The predictive ability of reactor modeling is limited by the accuracy of the rate constants used for gas phase reactions and the reactions at the surface. Over the last few years, Gallium Nitride has attracted significant attention due to its ability to produce blue light, and wide band gap transistors. This poster presents a "first principles" approach to the calculation of the reaction rates for gas phase and surface reactions occurring during MOVPE of Gallium Nitride using trimethylgallium and ammonia as precursors. Our approach uses fundamental concepts of statistical mechanics and transition state theory in conjunction with ab initio quantum chemistry method to calculate surface reaction rates. The gas phase rate constants were calculated in a function of temperature and pressure by combining quantum chemical method with the quantum RRK (QRK) theory. To calculate the pre-exponential factors for adsorption and desorption reactions of various gas phase species, a loose transition state is assumed where the adsorbate moves over the surface with a two-dimensional translational motion. Moreover, the appropriate degrees of freedom have been assigned for the adsorbates at the gas phase, transition states for adsorption and desorbed states in order to calculate the pre-exponential factor accurately. The activation barriers for surface reactions were either extrapolated from the analogous gas phase reactions or calculated using a cluster model. Calculated rate constants were then used for commercial reactor scale modeling of gallium nitride deposition. Modeling results exhibit excellent match with available experimental data.  

08.2  
THE EFFECTS OF INTERRUPTION TIMES ON HIGH In CONTENT InGaN/GaN QUANTUM WELL GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION.  
In recent years, InGaN/GaN multi quantum wells (MQWs) have received much attention as the active material in blue and green light emitting diodes (LEDs) and light diodes (LDs). However, despite the remarkable progress in device performance, comprehension of InGaN/GaN quantum wells is still a vigorous research field. The compositional fluctuation of In and V-defects in InGaN/GaN QW have been studied about their roles and origins by many groups. It has been controversial that the luminescence center in InGaN QW is originated from the presence of In-rich region or the self-formation of quantum dot (QD) and this localized states and V-defect are related to the high quantum efficiency. In this work, we investigate the effect of interruption time on the optical and structural properties of high In content InGaN/GaN QW. Especially we studied about the compositional fluctuation of In and V-defect using atomic force microscopy (AFM), photoluminescence (PL), high resolution transmission electron microscopy (HRTEM), and high resolution X-ray diffraction (HRXRD). All samples were grown on c-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD). InGaN/GaN QWs with interruption time of 0, 5, 10, 30, 60 sec were deposited after growing the 2µm thick InGaN layer at 1130°C. Our AFM measurements revealed that no significant increase of the pit size or number were not observed in the InGaN/GaN QW. This indicates that the interruption time didn’t affect on the V-defect formation. In our HRTEM examination, The dark contrast in InGaN/GaN QW indicated the QD like or In-rich region. The PL spectra measured at low temperature showed that the luminescence of QD like is much dominant than that of QW. The number and size of...
the growth structure depend on the thickness of overgrown GaN layer and the duration of flashing, which may be attributed to defect reduction. We investigated the samples by PL and different TEM techniques. We found that complements of small InAs QDs formed by InAs 4 ML deposition at 320±35°C usually contain dislocation dipoles. It should be noted that the dislocation core of dipoles always stays at the GaN/GaN interface. In some cases, a complete dislocation network was found in the non-flashed specimens. The defect structure formed in the vicinity of InAs QDs depends on thickness of overgrown GaN layer and flash parameters. The thermal flashing of samples with thin GaN overlayer thickness results in almost complete elimination of structural defects (mikto-macromolecular dislocation network, dislocation dipoles) and considerable increase in PL.

8.6 GROWTH MODELING OF InAs(001) ON THE BASIS OF Ab Initio DFT, STM AND RHEED. Frank Grozer,4, Michael Barvanov-Carter,4, Christian Reich,7, Richard Ross,6, James Owen,4, Jenna Ziek,2; UC Los Angeles; 4HRL Laboratories.

Growth simulations of III/V semiconductors can give significant insight into basic physical mechanisms and provide improved growth methods leading to higher quality in device applications. Due to their complex reconstructions, simulating III/V semiconductor growth on relevant length and time scales is a challenging task and makes approximations necessary. On the other hand, to be predictive and to span a wide range of validity, high accuracy in the description of the reaction processes is crucial. We combine theory and experiment, in particular ab initio density functional theory with scanning tunneling microscopy and reflection high energy electron diffraction experiments to build a high resolution kinetic Monte Carlo growth model of InAs(001) homoepitaxy valid for growth on singular and vicinal surfaces under a large variety of growth rates in different different As pressures and temperatures. Thermodynamical equilibrium properties including phase transitions between different reconstructions are given within the growth model solely by ab initio calculations, the remaining parameters describing the growth kinetics, namely the In transition energy and prefactors, are determined by comparison to desorption experiments and island size distribution. With our model we are able to explain non-intuitive trends with increasing As pressure, to step on vicinal surfaces, and large islands in the low coverage regime, in excellent agreement with STM observations.

8.7 EVOLUTION OF COHERENT InAs QUANTUM DOTS ABOVE THE coherent CRITICAL THICKNESS WINDOW BY METALORGANIC CHEMICAL VAPOR DEPOSITION. T.S. Yeh, J.R. Coleman. Semiconductor Laser Laboratory, Urbana, IL.

The evolution of Stranski-Krastanow grown InAs quantum dots on GaAs was examined by varying the deposition thickness and growth interruption times. We have grown coherent InAs quantum dot layers with depositions within and above the theoretical monolayer coverage window for defect-free quantum dot formation. By metalorganic chemical vapor deposition. As with other metalorganic chemical vapor deposition systems, a low V/IH ratio during growth is critical to the formation of fully coherent islands. The resulting dots of densities exceeding 4.8×10^8 cm^-2 were found to have a lower critical thickness of formation and a smaller diameter than previously reported. By correlating photoluminescence and transmission electron microscopy of quantum dots capped at various growth interruption intervals, we found the growth interruption time to be a critical factor in generating defect-free quantum dot ensembles for coverages exceeding the critical thickness. Densities exceeding 1×10^9 cm^-2 for coherent layers of InAs Quantum Dots grown by Metalorganic Chemical Vapor Deposition in the theoretical critical thickness for APMOCVD and MOCD for specific time windows with no change in incoherent dot densities. Our results imply that the incoherent dots are generated only after the coherent dot density reaches a minimum density whereupon the remaining source material from the wetting layer becomes incorporated into dislocated quantum dots. This nucleation rate difference between coherent and incoherent dot formation allows us to engineer unique, metastable quantum dot structures at and above the window for defect-free quantum dots.

8.8 GROWTH OF COMPOUND SEMICONDUCTORS IN NANOFLUIDER SIZE CHANNELS OF POLYMERS. R. Engelhardt and R. Koenen, R, Ionenkamp, Hahn-Meitner Institut, Berlin, GERMANY.

Using solution growth techniques we have prepared compound semiconductors as vertical columns in nanometer diameter channels in
polymer foils. The polymer foils are first exposed to irradiation by heavy swift ions, then exposed to an appropriate etch solution. The ion irradiation leads to the formation of narrow ion tracks of nearly amorphous structure. Upon exposure to the etch solution these regions etch preferentially. Vertical channels of well defined geometry with diameters as small as 4 nm are formed in the etching process. We demonstrate the controlled growth of polycrystalline semiconductors in these channels. Upon removal of the polymer vertically aligned semiconductor columns with large aspect ratios and nanometer diameters remain. Device applications will be discussed.

08.9
STRUCTURAL EVOLUTION OF PSAMDOMPHIC InSb
MOLECULAR-LAYER ON Si(001) AND Si(111) SUBSTRATES.
H.V. Rao, D. Goswami, T. Tambo, C. Thayumanavan, Toyama University, Toyama, JAPAN.

Growth of InSb on Si substrates is very difficult due to the presence of over 10% lattice mismatch. This mismatch is much larger than the theoretically predicted 12.14% mismatch for the pseudomorphic growth. This large mismatch results in the formation of 3D islands much before the completion of first InSb molecular layer. Recent results of InSb growth on GaAs showed that at a nominal coverage of about 90ML, InSb covers whole of the GaAs surface (n ~ 15% mismatch). In and Sb are well-known surfactants in the Si industry, which are known to modify the growth kinetics on Si surface. Present study illustrates how the In-induced surface reconstructions of Si substrates can be used to achieve pseudomorphic growth of InSb on Si. Sb adsorption on Si(001), In(4x4) reconstruction at 280°C results in the formation of pseudomorphic InSb on Si. We report a new reconstruction of InSb, where the large unit cell of 4x3 reconstruction acts as a nucleation site. The large strain due to the lattice mismatch seems to have relieved by the formation of periodic defect structures. This 2x8 structure can be compared to the InSb(001) 2x8 reconstruction. On the other hand, Sb adsorption on Si(111)-4x4(4x3) completely replaces the Si-In bonds by Si-Sb bonds. This replacement seems to soften the poorly reactive Si-Sb interface with the formation of well ordered Si(111)-4x2(2x1) reconstruction at 300°C (Sb deposition on Si(111)-7x7 surface below 550°C produces only disordered phase). The replaced In atoms reorder on this 2x1 phase to form a pseudomorphic InSb molecular layer with 2x2 structure. Again, this structure is comparable to the InSb(111)-2x2 reconstruction. We detail the difference in the structural evolution of Si(001)-InSb(001) and Si(111)-InSb(111) molecular layers.

08.10
INFLUENCE OF TEMPERATURE AND ION KINETIC ENERGY ON SURFACE ROUGHNESS OF THIN FILMS FABRICATED BY DUAL PLASMA DEPOSITION.
L.P. Wang, K.Y. Yu, X.B. Tian, H.Y. Tseng, and P.K. Chu, City Univ. of Hong Kong, Kowloon, Hong KONG.

The surface roughness of thin films affects the crystalline properties as well as their applications and is preferably as small as possible. In our experiments on the fabrication of CeOx thin films on Si(100) substrate by dual plasma deposition, we investigate the influence of the substrate temperature and ion kinetic energy on the surface roughness. The surface roughness decreases with increasing substrate temperature, possibly due to enhanced diffusion of the adatoms. A higher ion bombardment energy has a similar effect and it is also believed to be related to the surface diffusion of adatoms. We have also found that when a DC voltage is applied to the substrate and the film is thick with a high electrode breakdown, the surface is rough. On the other hand, when the film is thin and the applied DC voltage can cause breakdown in the film, the film exhibits smaller roughness. We will present our experimental results as well as a mechanism to explain the data.

08.11
MICROSTRUCTURE OF ORGANIC THIN FILMS GENERATED BY ELECTROLEUCINESCENT MOLECULES STUDIED BY GRAZING-INCIDENCE X-RAY DIFFRACTION.
Deftel M. Smidt, CHESS, Cornell Univ, Ithaca, NY; Ed Kostad Jr, James G. Siedenick, Florida State Univ, Physics Dept, Tallahassee, FL, Hisao Yamag, Kobe University, Dept of Electrical Engineering, Kobe, JAPAN.

Recently thin films of small aromatic molecules have received a lot of attention for their potential use in light-emitting diodes and organic transistors. The advantage of small molecules over the commonly used light-emitting polymers is that they can be grown in crystalline form and their electronic and optical properties can thus be better understood and controlled. Single-crystal allene films have been found to have narrower optical emission spectra and to emit polarized light. Furthermore it is hoped that single crystalline films can be grown with smaller defect densities than polycrystalline films and have a longer lifetime in devices. An important step in the development of crystal growth techniques is the characterisation of the microstructure of such films. We have employed synchrotron-based grazing-incidence x-ray diffraction (GIXRD) to investigate films of polyfluorene and POPOP which were grown by molecular beam epitaxy on alkali halide surfaces. GIXRD allows to identify various crystalline phase growing simultaneously, different orientations of the surfaces of the crystalline films, as well as epitaxial alignments of the crystals with respect to the substrate, even in very complex systems. Furthermore, the domain structure of the film can be characterized, which is a dependent on both the substrate symmetry as well as the symmetry of the molecules forming the film. Applications of the synthesized crystalline films have been shown in recent results on thin films of p-4P on NaCl(001) and POPOP on KCl(011).

08.12
STUDY OF DIFFERENT PHASES IN n-C: H:N THIN FILMS DEPOSITED BY PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION: A COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL DATA. F. Antonelli, L. Valentini, Engineering Center, Perugia Univ, Perugia, ITALY; A. Continenzi, L. Locci, S. Santucci, L'Aquila Univ, Dept of Physics, L'Aquila, ITALY.

The growth of nitrogen doped amorphous carbon compounds (n-C:H:N) thin films is an important issue in the material science because of their interesting properties, such as high hardness, low friction coefficients, chemical inertness. These films are usually prepared by means of Ar+ plasma assisted chemical vapour deposition. During the growth of these materials an important effect is the formation of different phases because of the use of high energy ions. The aim of this work is to study the growth of (n-C:H:N) films deposited with plasma decomposition of CH4:N2 and CH4:N2/Ar mixtures, with different methane and nitrogen flows. In order to understand the stoichiometry and the possible phases present in the compounds, we compared the X-ray and Soft X-ray photoemission valence band spectra with an n-initio study using the full-potential linearized augmented plane wave (FLAPW) method on some selected ordered C:N phases such as C3N4, CN diamond and graphite.


08.13
APPARATUS DEVELOPMENT FOR DIAMOND SYNTHESIS FROM ACETONE VAPOR WITH LOW ENERGY CONSUMPTION.
Fumitomo Onishi, Rie Hayashi, Yoshiki Takagi, Division of Materials, Tokyo Univ. of Science & Technology, Yamagata-ken, JAPAN.

We synthesized diamond via gaseous phase of vaporized acetone. Molecular acetone decomposes to two methyl radicals with activation. We propose here a new method for diamond synthesis with these methyl radicals from molecular acetone. With this method, we successfully synthesized diamond nanoparticles with shorter experimental time. With liquid carbon source, such as acetone, substitutional impurities will be easily incorporated in synthesized diamond thin film for the electronic device applications.

08.14
DIAMOND SYNTHESIS ON OXIDE SUBSTRATES. Rie Hayashi, Fumitomo Onishi, Yoshiki Takagi, Division of Materials, Tokyo Univ. of Science & Technology, Yamagata-ken, JAPAN.

Recently, many results were reported by many institutes and companies all over the world for diamond particles or thin films synthesized on crystalline substrates, such as molybdenum, silicon etc. But diamond on oxide or amorphous substrates, were rarely reported. In this study, we used oxide materials as substrates, for example, quartz glass, borosilicate glass (PYREX), nihima, etc. We used unique apparatus of diamond synthesis. It is on our completely closed system, no reaction gas was introduced to the chamber and no reaction gas was evacuated from the chamber. Graphite rod w.r.t. the carbon source, mounted the center the chamber, about 3-mm under the rod, the oxide substrates were set. Hydrogen gas was introduced into the reaction chamber with the suitable initial pressure, and then sealed. Graphite rod was heated and controlled with Joule heating. The typical reaction time was 40 min. With SEM photographs, crystal shaped particles were observed. And with Raman spectrum, Raman peaks were assigned as typical diamond peaks. The results have been duplicated. With these results, we clearly confirmed that the deposits on oxide substrates were diamond particles. And we compared the results with these of unique closed system and conventional flow system.

08.15
SYNTHESSES OF DIBLOCK/SILICA FILMS WITH REGULAR AND RANDOM MICROSTRUCTURES OF LARGE COLUMNS AND PARTICLES ON THE PARTICLE LENGTH SCALES BY SOLEVANT EVAPORATION-INDUCED SELF-ASSEMBLY OF POLYSTYRENE-BLOCK-POLY(ETHYLENE CO-PROPYLENE)


Mesoscale structured silica films with large characteristic length scales were synthesized through an evaporation-induced self-assembly procedure, employing amphiphilic polystyrene-block-poly(ethylene oxide) (PS-b-PEO) diblock copolymers as structure-directing agents. The synthesis process begins with a dilute homogeneous solution of a silica precursor, PS-b-PEO, and methanol in tetrahydrofuran (THF) and water. During film formation, THF preferentially evaporates, accordingly, the species in the depositing film increasingly concentrate and the solvent volume fraction for the diblock progressively decreases. At some critical point, coarsening of both the PS-b-PEO diblock and the silicate starts. Subsequently, liquid-crystalline mesophases are obtained. From one identical copolymer sample, diblock/silica films with different mesoscale structures can be synthesized. As the volume ratio of the silicate increases, morphologies of the mesostructures change progressively from regular, through lamellar, to inverted. For the diblock/silica films with regular mesophases, copolymer removal produces mesoporosity; the pore size is controlled by the molecular weight of the diblock (at a constant volume ratio of the diblock to silica). The present system is believed to be the first to yield amphiphile/silica films with regular and reverse mesoporosity, as well as multilayer vesicular mesostructures, through solvent-evaporation-induced self-assembly (EISA). The present process of self-assembly goes from dilute to concentrated solution regimes; a comparison of the present system and related systems of diblock/silica dispersed in dilute solution in bulk is presented. A range of similarities of the three systems, such as morphogenetic effects of effective volume ratios of the two blocks, is highlighted. Furthermore, the ready formation of the diblock/silica films with multilayer vesicular mesostructures is discussed.

OS.16 AFM STUDIES OF CARBOSILANE DENDRIMER CHEMISTRY ON MICRON SCALE AND SILICON SURFACE. Zhongzheng Xiao, Xiaobin Deng, Aurelie Mayeux and Chengzhi Ca University of Houston, Dept of Chemistry, Houston, TX.

The absorption and binding of SiC or ethynyl groups carbosilane dendrimer on micro and silicon substrates have been investigated by atomic force microscopy (AFM). Multilayer, monolayer and monodispersion images of dendrimer molecules have been obtained on micro scale by AFM. From AFM images, it was observed that the shape of the individual dendrimer was nearly spherical disk and the apparent size was about 20 nm in diameter that correlates the shape of SiC. The binding of dendrimer onto oxidized silicon surface was very strong, which is due to “multipoint binding” of dendrimer that results from the formation of a large number of Si-O bonds at the interface, and annealing could significantly promote such binding. The contact angle of dendrimer monolayer is up to 94°, indicating the preferential adsorption of the end groups of dendrimer and oxidized silicon surface than exposing a hydrophobic core to the surface.

OS.17 THE IMPROVEMENT OF THIN POLYMER FILM PROPERTIES THROUGH PLASMA IMMERSION ION IMPLANTATION AND DEPOSITION TECHNIQUE. Eldonie C. Rangel, Nilson C. Cruz, Rogério P. Mota, Roberto Y. Hinai, Maurício A. Akoggi, UNESP, Dept of Physics and Chemistry, Guaratinguetá, SP, BRAZIL.

Plasma Immersion Ion Implantation and Deposition (PIID) is a powerful technique that enables ion bombardment during the deposition process, rendering unique characteristics to the plasma deposited films. Simultaneously to the plasma establishment, high voltage negative pulses are supplied to the substrate holder. During the off-time of the pulses, species from the plasma are deposited onto substrate as physical vapor deposition (PVD), in the case of the PIID, ions from the plasma are accelerated to the biased electrode and implanted in the samples, providing in situ modifications. This work describes the influence of the pulse frequency, \( \nu \), on the chemical, optical and mechanical properties of polymer films deposited/bombarded by plasma. The glow discharges employed in this study were excited by radiofrequency power (13.56 MHz, 60 W) in acetylene and argon gas mixtures. Negative pulses (25 kV) were supplied to the substrate holder at different frequencies. Infrared and ultraviolet-visible spectroscopy were respectively employed to investigate the chemical structure and the optical constants of the films. Polymer wettability was determined through contact angle measurements. The result was then the modification of the surface to oxidation was studied by its etching rate in oxygen plasma. Hardness measurements were performed using the nanindentation technique. It was observed that the film deposition rate increases with increasing \( \nu \). Increasing after this. The molecular order and the chemical composition were also modified in the bombarded samples. Increasing the pulse frequency resulted in an improvement in the oxide content of the films and in their hardness. Further, the pulse frequency was also observed to influence the film morphology, with the film being more compact and denser at lower frequency.

OS.18 CHARACTERIZATION OF CHEMICAL AND SENSORIC PROPERTIES OF ION-BEAM MODIFIED POLYETHERSULFONE LAYERS. Karin Salam, Klaus-Jochen Ethehorn, Frank Simon, Institute of Polymer Research (IPF), University of Stuttgart, Germany, and Guenter Gunther, Rainer Suchmann, Gerald Gerlach, Dresden University of Technology, Institute for Solid State Electronics, Dresden, GERMANY.

Thin chemically modified polyether sulfone films (PE) are increasingly important for application as functional layers for new microelectronic sensors. To modify such polymeric structures the ion implantation is a prefered method. In this work, we present results of an ion-beam modified polyether sulfone (PE) surface layer. To measure the changes in the chemical structure of the PE surface layer, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used. The combination of these analytical methods gives a complete picture of the main processes in the layers. Thus the results of vibrational and X-ray photoelectron spectroscopy indicate that in dependence of dose and energy of implanted ions the sulfone bonds are destroyed and carbon-rich, amorphous and graphitic-like structures are formed. The morphologies (10% decrease) and the specific refractive index of polymer layers from about 1.6 to 2.0 caused by the implantation at high energy and dose (180 keV, \( 10^{-10^6} \) ions/cm²) were studied using scanning electron microscopy. To fit the ellipsometric data we used a suitable optical model which represents the physical reality of the samples satisfactorily. Second, sensoric properties of PES films especially the swelling behavior in dependence on relative humidity were investigated using a corresponding biocompatible polymer sensor. The influence of ion-beam induced modification on moisture uptake was determined by Freundlich's coefficient. Results concerning the stress-strain-relationships and the change of the electrical properties dependent on dose and energy of implanted ions are also presented.

OS.19 STRUCTURE MODULATION AND STRAIN RELAXATION MECHANISMS IN FERROELECTRIC THIN FILM. Laurent Lihache, Lab. Rech. UMMT UTC-CNRS, 1 UPT, Amiens, FRANCE; Vladimir Lermont, LPM, CNRS, Univ. of Montpellier 2, Faculty of Physics, FRANCE; Sergei Rochev, Univ. of Rostov on Don, Faculty of Physics, RUSSIA; Jean-Francois Reichenb, Lab. Rech. UMMT UTC-CNRS, Univ. of Tech. of Compiègne, FRANCE.

This study investigates the possible stress relaxation mechanisms in (PZT) epitaxial ferroelectric thin film single crystalline thick substrate. The main attention is paid to the dielectric, thermodynamical and mechanical properties of the nano-material. The proposed analysis taken into account the inhomogeneous filmsubstrate coupling together with the specific 2D mechanical boundary condition and the total strain relaxation due to this dislocations. For this goal, we develop a phenomenological model which includes a detailed crystallographic analysis of the inhomogenous morphology and following thermodynamic consequence. The model is based on the experimental data which reveal a coincidence lattice in the interface. It allows us to consider the transformational properties of an induced inhomogenous modulation arising in the film due to its coupling with the substrate. The modulatin is then related to one of the irreducible representations of the space group Gf of the ferroelectric material which composes the nano film. It permits to describe the thermo-electro-mechanical problem in terms of the Gf dynamical groups. The geometry between internal variables, namely the order parameter of the structure, stress tensor and electrical polarization vector. In order to obtain the stability regions in the thickness-temperature plane and corresponding film microstructures for different ferroelectric states formed during the deposing process and the successive return to room temperature, we perform the energy minimization. The resulting phase diagram shows different regimes of film growth : i) in the ultrathin films the surface formation mechanism faces the phase with non-trivial unit cell multiplication and the polarization direction perpendicular to the substrate, ii) for the films with the thickness higher than 100 nm 3D-clamping stabilizes usual c-domains and iii) for the intermediate thicknesses, several c-type states can become stable. A numerical modeling of the residual strain level in the film is also proposed for three qualititatively different thicknesses.

OS.20 EFFECTS OF ROUGHNESS OF SUBSTRATES AND OXYGEN
The c-axis preferred orientation of the piezoelectric film is the most important factor in manufacturing of piezoelectric devices. The effects of roughness of substrates and oxygen content were investigated on c-axis preferred orientation of ZnO films deposited by radio frequency (rf) magnetron sputtering. The total sputtering pressure was 0.3 Torr, and the oxygen partial pressure was varied from 0% to 70%. The rms roughness of the used substrates were 1.27, 1.71, 21.1, and 65-118 Å. The crystalline structure and the angular spread of (002) plane normal to the substrate were determined by x-ray diffraction, and rocking curve analyses. The crystallinity and the c-axis preferred orientation of ZnO films strongly depended on the oxygen content and the surface roughness of the used substrates. The deposited ZnO films had better crystallinity and higher c-axis preferred orientation on the smoother surface substrate. 

OS 23

\textbf{FIBERIZATION OF ZnO THIN FILMS BY FACING TARGETS SPUTTERING SYSTEM.} M. J. Keum, S. Y. Yang, H. S. Kong, J. H. Kim, Kyungwon University, School of Electrical 

& Electronic Engineering, Konyung-go, Korea; H. S. Han, Shinjuku College, Dept of Electrical Engineering, Chugunung KOREA; S. Nakogawa, Institute of Technology, Dept of Physical Electronics, Tokyo, JAPAN.

ZnO thin films were prepared in pure O₂ gas on glass substrate by Facing Targets Sputtering (FTS) apparatus which can control sputtering parameters in wide range. It is important for changing the energy of sputtered atoms because of the crystalllographic characteristics of ZnO thin film changed with sputtering parameters.

In order to change the energy of sputtered atoms, we controlled the discharge (0.1-0.8A) and the O₂ gas pressure (0.5-2.0Torrs). Also, the influence of substrate temperature (RT-300°C), discharge current and film thickness on the properties of the films have been investigated. The c-axis orientation (Δφ₀) was 35° at substrate temperature 300°C, discharge current 0.4A, working gas pressure 1mTorr, and film thickness 0.5μm. When the film thickness is over 1μm, c-axis orientation (Δφ₀) of ZnO thin film showed good with increasing working gas pressure or decreasing discharge current. The c-axis orientation (Δφ₀) of ZnO thin film was 3.3° at substrate temperature 200°C, discharge current 0.3A, working pressure 1mTorr and film thickness 3.5μm.

OS 24

\textbf{REMOTE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF TiO₂ FILMS FROM TiF₄-TETRASOPROXIDE.} Makoto Nakamura, Shinichi Kato, Toru Aoki, and Yoshinori Hazumaki, Graduate School of Electronic Science and Technology, Research Institute of Electronics, Shinshu University, Zoshu, JAPAN.

TiO₂ films have intensively been investigated as photocatalytic and hydrophilic material under UV light irradiation and applied as anti-fog mirror for automobile. Especially, it is known that anatase type crystalline films show good properties for this purpose. In this study, TiO₂ films were prepared by remote plasma enhanced chemical vapor deposition (CVD) technique using titanium tetrasopropoxide (TTIP, Ti(OPr₂)₄). TTIP is preferable because it incorporates no corrosive component in contrast with the compounds of hydrogen such as chlorides or bromides. In the process including high density ion of 10⁴/cm³, deposition rate was strongly depended by substrate temperature. Negative value of estimated reaction enthalpy in this process meant that adsorption and desorption reactions were dominant for surface reaction of TiO₂ deposition. The rate selection process was supposed that energetic species existed enough to dissociate TTIP molecules in gas phase and TTIP transport rate limited deposition rate in this regime. Deposition rate increased up to 500nm/min as TTIP transport rate was increased. The films deposited at low substrate temperature of less than 200°C were amorphous by x-ray diffraction spectra. From FT-IR spectra it was revealed that these films included a large amount of Ti-OH group. In spite of their amorphous state, these films were sensitive to UV light irradiation and showed highly hydrophilic properties. It is suggested that remote plasma enhanced chemical vapor deposition of TiO₂ films is effective for the preparation of hydrophilic surface on plastic substrates. Deposition mechanism and high specificity of the amorphous TiO₂ film was discussed in the presentation.

OS 25

\textbf{TITANIUM MONOXIDE FILMS ON Cu AND Cu OXIDE GROWTH MODE OF ROOM-TEMPERATURE DEPOSITED FILMS ON Cu AND EFFECT OF Cu OXIDE.} V. M. Fournald, C. G. Guinn, C. Herrera, R.A. Zebolt, Center for Inorganic Nanoscience, Department of Materials Science and Engineering, University of California, Davis, CHILE.

Polycrystalline copper films >100 nm thick were evaporated on silicon wafers under ultrahigh vacuum conditions leading to an rms roughness of the films ~2 nm. Some of these substrates were oxidized in air to obtain a native copper oxide. TiO₂ films were subsequently deposited onto the “clean” and oxidized copper films from a resistively heated tungsten boat, in situ, at room temperature. The
films exhibited good adherence and were amorphous. XPS also revealed that the TiO films were contamination-free and that the TiO coating was continuous. The TiO was formed on the copper substrate from Cu(II) into Cu(I) or Cu(0) and transformed the TiO into TiO$_2$ at the interface. No reaction between the copper and the TiO was detected. The low-energy ion scattering spectra (LEIS) of the TiO films up to several hundred microns thick showed that the TiO coating layer is continuous, thus implying that the TiO grows by the nucleation of islands even at room temperature. Complete coating of the copper film, as revealed by LEIS, was assured only for TiO deposits above 5 nm.

**OS.26 ELECTROCHEMICAL PROPERTIES OF SnO$_2$ THIN FILMS DOPED WITH Bi AND Si FOR NEGATIVE ELECTRODE OF MICROBATTERY. Young-Hi Kim, Hoon-Soon Moon, Kwang-Sun Ji, Hanyang Univ, Div of Materials Science and Engineering, Seoul, KOREA; You-Kee Lee, Ulsan Univ, Dep. of Semiconductor Engineering, Kyungsung, KOREA; Jong-Won Park, Hanyang Univ, Div of Materials Science and Engineering, Seoul, KOREA.**

Tin oxide has been proposed as a promising alternative anode material for microbatteries. It has been reported that its theoretical volumetric capacity is four times larger than that of carbon-based materials, although its gravimetric capacity is twice as large. In this experiment, an optimal amount of Si dopant added to SnO$_2$ film was determined. Then, Bi was added to Si doped SnO$_2$ films which were prepared with e-beam evaporation to improve both the cycle performance and the reversible capacity. The effects of Si and Bi addition to the SnO$_2$ films on the microstructure of the thin films deposited on Al substrates were investigated. The films with addition of Si only exhibited reductions in aggregation of tin particles and formation micro-cracks, especially at SnO$_2$/Si. However, there still remained cracks, which induce capacity loss during cycling. To improve the film microstructure and to avoid cracks, Bi was added to Si doped SnO$_2$ films. This resulted in high reversible capacity of 400–500 μAh/cm$^2$ at 200th cycle. The films doped with Bi and Si were found to be ill-defined and featureless without noticeable particle aggregation and cracks. Moreover, the films, which underwent cycling tests showed again aggregated tin particles and re-appearing cracks, which induce cell failure during cycling. We believe that some types of Li-Bi phases as mixed-conductor matrices may improve the cycle life.

**OS.27 LUMINOUS EFFICIENCY OF AC PLASMA DISPLAY PANELS WITH MgO$_2$-TiO$_2$ PROTECTIVE LAYERS. Younghwan Kim, Bakhwan Kim, Yongik Lee, Sung Hoon Chang, Jong-Won Park, Hanyang University, Div of Material Science and Engineering, Seoul, KOREA.**

Development of the protective layers with higher secondary electron yield than that of the conventional MgO is necessary to attain both lower driving voltage and higher luminous efficiency in AC plasma display panels. TiO$_2$ was added to the pure MgO in order to improve the electrical characteristics of AC plasma display panels using electron beam evaporation. As the [TiO$_2$]/(MgO + TiO$_2$) ratio in the starting materials increased, the ratio of [Ti]/[Ti + Mg] and the ratio of metal to oxygen of [Ti + Mg]/O in the films increased gradually, which might result in the change of the secondary electron emission yield of MgO-TiO$_2$ films. The secondary electron emission yield of MgO-TiO$_2$ films was found to be larger than that of the conventional MgO protective layer. The luminous efficiency of the panel with MgO$_2$TiO$_2$ protective layer was much higher than that of the panel with MgO protective layer, probably due to its lower discharging voltage. The increase in the luminous efficiency and the decrease in the driving voltage were in good agreement with the result of secondary electron emission yield as expected.

**OS.28 HETEROEPITAXIAL AND POLYPYRROLE INDUCTION OXIDE FILMS PREPARED BY OXYGEN ION ASISTED DEPOSITION. Jin-Sik Cho, Younggun Han, Seon-Ju Kwon, Young-Won Kim, Seok-Kwon Koh, Korea Institute of Science and Technology, Thin Film Technology Research Center, Seoul, KOREA.**

Heteroepitaxial and polypyrrole growth of undoped indium oxide films was carried out on polished YSZ (80/20) and glass substrates by oxygen ion assisted deposition. The oxygen ion energy was varied from 60 to 500 μeV during indium thermal evaporation. The crystallinity and microstructure of the films were closely related to the oxygen ion energy bombarded on the growing surface. Domain structure and preferential orientation in the [100] direction were obtained in the films deposited at 60 μeV. Upon increasing the beam energy to 500 μeV, the domain structure was changed into the grain structure. Depending on the range of ion beam energy, the main effect of energetic ions on the growing surface of the film may be divided into two cases: in the first case, the enhancement of the creation of additional nucleation sites by lattice damage. The dependency of electrical properties of the films on the crystallinity and microstructure will be discussed.

**OS.29 YTTORIA STABILIZED ZIRCONIA THIN FILMS PROCESSED BY COMBUSTION CHEMICAL VAPOR DEPOSITION. Ziqing Xu, Qingwei Wei, Dept of Advanced Materials and Smart Structures, North Carolina A&T State University, Greensboro, NC.**

Yttria stabilized zirconia (YSZ) is a conductor of oxygen ion. It has been widely used as electrolyte in solid oxide fuel cells. Due to its relatively low ionic conductivity, thin film of YSZ is favored in order to minimize the current path in the electrolyte. Combustion chemical vapor deposition (CCVD) has been used to deposit thin films of diamond, especially many kinds of oxides, such as Al$_2$O$_3$, Cr$_2$O$_3$, SiO$_2$, YBCO and YSZ. Among techniques to prepare the YSZ electrolyte thin film for fuel cells, CCVD in open atmosphere has potential of high deposition rate and low operational cost. We have established a liquid fuel CCVD system. Basically, this system consists of a quaternary HPLC pump, an atomizer, a pilot flame and a substrate cooling/holding supporter. Substrate is placed near or at the end of the nozzle flame. A series of parametric experiments have been conducted. Zirconium 2-ethylhexanoate and yttrium 2-ethylhexanoate dissolved in toluene are used as reagents. Thin films are deposited on Si(100) and MgO(100) substrates. Effects on morphology and microstructure of factors such as concentration of solutions, substrate temperature and position of the substrate in the flame are thoroughly investigated to obtain uniform and dense films. The correlation between the reagent composition and film composition is also studied in order to get cubic phase zirconia in room temperature. The dependence of high temperature annealing on the microstructure is also studied. The phases of the films are characterized by X-ray diffraction. The morphologies and microstructures of them are studied with scanning and transmission electron microscopy.

**OS.30 FORMATION OF YCrO$_3$ THIN FILMS USING RADIO-FREQUENCY MAGNETRON SPUTTERING METHOD FOR A WIDE RANGE THERMOELECTRIC APPLICATION. Sang-Han Kim, Jin Hyek Lee, Jong-Hun Moon, Chonnam National University, Dept of Inorganic Materials Engineering, Kwangju, SOUTH KOREA; Byung-Tak Lee, Chonnam National University, Dept of Metallurgical Engineering, Kwangju, SOUTH KOREA.**

YCrO$_3$ thin films were prepared on thermally oxidized silicon wafers by radio-frequency magnetron sputtering method for their potential use as wide range thermoelectric materials. Microstructure and crystalinity of thin films, deposited and then post-annealed at various temperatures up to 600°C/1h, were investigated using transmission electron microscopy and x-ray diffractometer. It was observed that as-deposited sample has an amorphous phase. Mixtures of an amorphous phase and a crystalline phase were observed in a sample annealed at 600°C/1h, and completely crystallized YCrO$_3$ thin films were observed in samples annealed at above 700°C/1h. Resistance change of YCrO$_3$ thin film was studied as a function of temperature. A YCrO$_3$ thin film, deposited at 200°C with RF power of 100W, working pressure of 4 mTorr, an Ar/O$_2$ ratio of 25%/75% and then annealed at 800°C/1h, showed a linear characteristic in the log i vs 1/T plot in the temperature range between 300°C and 800°C, showing potential for developing a temperature sensor.

**OS.31 FORMATION OF A Co$_2$O$_4$ TOP LAYER IN SiO$_2$ COBALT CONTAINING COATINGS SOL-GEL OBTAINED. H. Tottorez-Hurtelé, A. Ramous-Mendez, A. Mendoza-Galvan, J. Gonzalez-Hernandez, Centro de Investigación y de Estudios Avanzados del IPN, Unidad Querétaro, MEXICO; B.S. Chao, Energy Conversion Devices, MI.**

We have prepared SiO$_2$ coatings containing cobalt by the sol-gel method on glass substrates. It has been found that in coatings with higher cobalt content, the formation of a Co$_2$O$_4$ top layer begins at decreasing under thermal annealing in air. We have studied coatings with a Si to Co nominal atomic ratio of 1.3 with optical, x-ray and Auger depth profiles measurements. Thermal annealing were performed by 10 min at different temperatures from 300°C in steps of 50°C in air under thermal annealing at 400°C at different times from 0 to 240 min were carried out. From the x-ray diffraction patterns the cubic spinel structure of Co$_2$O$_4$ was detectable. The reflection and transmission optical spectra in the mid-infrared temperature range were also measured with an air Co$_2$O$_4$/SiO$_2$/Co$_2$O$_4$-substrate system. From this, the cobalt oxide thickness was obtained as a function of annealing parameters, temperature and time. For the temperature range studied, it was found an activation energy of 0.11 eV for the cobalt oxide growth, from an Arrhenius plot. The layer thickness follows a
Electrode characteristics of sputtered lithium manganese oxide films with diamond-like carbon top layer. Hye-Soo Moon, Kwang-Sun Ji, Hanyang Univ, Div of Materials Science and Engineering, Seoul, Korea; Won-II Cho, Young-Soo Yun, Korea Institute of Science and Technology, Seoul, Korea; Jong-Young, Hanyang Univ, Div of Materials Science and Engineering, Seoul, Korea.

There have been increasing interests in lithium rechargeable batteries, especially microbatteries, with rapid development of potable electron equipments and MEMS (Micro electromechanical systems) technology. In this work, lithium manganese oxide, as a strong candidate for the battery material, which is more abundant, stable in ambient state and less toxic compared to other oxides such as lithium nickel oxides and lithium cobalt oxides, was deposited by rf magnetron sputter. The effect of thermal treatment on the microstructure and electrode characteristics of lithium manganese oxide cathode was investigated. In operation of lithium-ion microbatteries, battery failure could be caused by electrode/electrolyte interface reaction, internal stress, degradation of electrode and electrolyte materials during charging/discharging process and so on. In this research we focus on interface reaction problem such as internal resistance which would affect the cyclability and lifetime of microbattery. In order to reduce the interface reaction during operation, we introduce DLC (Diamond-Like Carbon) film that has high electrical conductivity, mechanical hardness and chemical stability. DLC film was deposited on sputtered lithium manganese oxide electrode by ECR CVD (Electron Cyclotron Resonance Chemical Vapor Deposition). Before DLC film deposition, post thermal treatments were adopted to gain proper crystallization of spinel lithium manganese oxide. The crystal structure of the samples after and before cycle tests was characterized by X-ray diffraction, surface analysis was done by XPS and AFM. The bonding diameters of all films were performed by cut-off voltage (4.2-3.0 eV) and current density (50 µA/cm²). Impedance measurement was used to analyze the internal resistance of the electrode.


Tungsten trioxide (WO₃) is a wide gap n-type semiconductor and is the subject of an intense both theoretical and experimental studies because of its interesting applications, such as gas sensors towards different gases, like NO₂ and H₂S, and as electrochromic film. Many of these possible applications are mainly due to the oxygen vacancies. For example, in gas sensors, the gas species are adsorbed on the surface changing the concentration of the free electrons on the surface. These electrons are present on the surface because of the oxygen vacancies. The variation of this concentration modifies the electrical conductivity of the film. Similarly, the presence of stoichiometric WO₃ compounds, determines the optical properties of these films. An important parameter in the preparation of WO₃ thin films is the thermal treatment following the sample growth. For example it has been shown that the gas sensitivity and response time are strongly influenced by the annealing procedure, because of the phase transitions induced by the annealing. In this work the WO₃ surface chemical composition has been studied by means of high resolution soft X-ray photoemission spectroscopy. We have studied the surface properties of both as deposited samples and samples after annealing in air at high temperatures. Valence band and W 4f core levels have been analyzed on different samples positions and high resolution maps have been acquired. The valence band spectra have shown W 5d density of state at the Fermi level, indicating the presence of metallic tungsten on the surface. This has been confirmed by the W 4f spectra, which present both metallic and oxide contributions. The high resolution maps, obtained following both valence and core states, have clearly evidenced the presence non stoichiometric areas and of some metallic islands.

Surface topography of mixed oxide layers Au/Al₂O₃: mixed oxides of aluminum and gold on Si. G. K. A. N. M. N. S. Amikam, Inst of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia.

The thickness of the Au/Al₂O₃ layer used in the magnetic tunneling junctions FM1/Al₂O₃/FM2 is less than 2 nm, here FM1 is for the ferromagnetic layer 1 and FM2 is for ferromagnetic layer 2. In order to control the work function hetero junctions Au/Al₂O₃ layers were deposited on Si substrates by the physical vapor deposition technique. The deposition of Al₂O₃ thin films was performed either by co-evaporation of Al thin film or directly reactive deposition. In this presentation, the surface topography of Au and Al₂O₃ thin films will be extensively studied. The Al and Al₂O₃ thin films were deposited on Si wafer with or without buffer layer (Ta or TiN) by using pulsed magnetron sputtering under ultra-high vacuum system (UHV) at room temperature. The modulation DC pulsed frequency can be adjusted from 2 kHz to 20 kHz; a RF bias can be applied to the substrate during the deposition, the frequency of the RF source is varied from 30 kHz to 60 kHz, the Vpp value of the RF bias can be adjusted from 10 V to 100 V. The Al₂O₃ thin films are fabricated either by using reactive magnetron sputtering or plasma oxidation of Al thin film. The thickness of the thin films are characterized by standard x-ray diffraction using the Cu kα line [0.154 nm]. The surface topography is obtained by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Auger electron spectroscopy is used to examine the chemical composition of the Al₂O₃ thin films. The surface roughness of Al₂O₃ thin films is usually 0.2-0.5 nm, crystalline alumina thin films can be obtained after the samples are annealed at proper temperature. Very smooth Al₂O₃ thin film with roughness can be sputtered on Si wafer with a Ta buffer layer at 2 kHz; DC pulsed frequency and RF bias substrate biasing (Vpp ~ 20 V). The influence of the sputtering...
Zinc oxide and copper oxide are the basic ingredients for methanol synthesis catalyst research. This research showed that the growth of metal films between ZnO and CuO/20 domain were of great importance to catalyst surface activities. In this study, we used chemical vapor deposition (CVD) technique to prepare ZnO/CuO/20 phase intermixed thin films, and to investigate the growth characteristics of these films. The X-ray diffraction (XRD) analysis showed that the films were mixture of ZnO of Cu$_2$O and CuO. The SEM and XRD results indicated that the films were polycrystalline with a composite structure. A representative film had a continuous thin ZnO phase bottom layer, followed by a ZnO/Cu$_2$O interface area, and finally a Cu$_2$O grains. The SEM analysis of the films showed that the growth of Cu$_2$O phase in the ZnO/Cu$_2$O films was not uniform. The copper oxide was attacked by the weak bond of the grain boundary and the Cu$_2$O phase showed a more rapid growth. The copper oxide was formed by the oxidation of copper metal, and the growth of copper oxide was controlled by the boundary reaction rate. The copper oxide growth rate was found to be dependent on the boundary reaction rate and the temperature. The study showed that the growth of copper oxide was influenced by the temperature, and the growth rate was found to increase with increasing temperature. The copper oxide growth rate was also found to be dependent on the copper oxide grain boundary. The copper oxide grain boundary was found to be responsible for the observed growth rate. The study also showed that the copper oxide growth rate was dependent on the copper oxide grain boundary. The copper oxide growth rate was found to increase with increasing copper oxide grain boundary.

Vanadium dioxide (VO$_2$) thin films deposited on different sapphire substrates have been investigated using XRD, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The XRD analysis showed that the VO$_2$ thin films were composed of monoclinic phases. The XPS analysis showed that the VO$_2$ thin films were composed of VO$_2$(M) and VO$_2$(T) phases. The TEM analysis showed that the VO$_2$ thin films were composed of VO$_2$(M) and VO$_2$(T) phases.

We examine the structure and stability of an ultrathin ceramic film coating a metal substrate, specifically an α-alumina, Al$_2$O$_3$, film grown on nickel. This metal-ceramic interface may play a role in materials failure of contact combustion engine thermal barrier coatings, the engine is composed of a primarily nickel alloy, and the aluminum “coating” layer thicknesses with repeated thermal cycling due to oxidation of aluminum in the metal alloy. Accordingly, we study the effect of increasing aluminum film thickness on the nickel-alumina interface using periodic slab density functional theory within the generalized gradient approximation. Since nickel forms stable alloys with aluminum, it is not obvious whether the bonds between nickel and alumina will be Ni-Al, Ni-O, or both. Interestingly, our calculations indicate that the preferred bonding mode depends on the thickness of the alumina film. Namely, for an alumina layer thicker than the alumina appears amorphous and both Ni-O and Ni-Al interactions take place, while for two and three monolayers, Ni-O interactions decrease and Ni-Al bonds become more pronounced. By studying the effect of increasing thickness on the Ni-substrate, we observe a marked increase in the work of adhesion for thicker alumina coatings. Insight regarding the work of adhesion is provided through analysis of the nickel density of states and function value. Our findings provide a new atomistic explanation for the observed increase in spallation with increasing thickness of oxide layer (alumina) that forms during preparation and operational cycling of thermal barrier coatings. The thickest alumina layers energetically prefer inter-ceramic bonding over Ni$_3$Al$_2$O$_6$ interface formation. Connections to metal-catalyst oxide support interfaces are also discussed.

Electrical Characterization of Carbon-Doped Th$_{2}$O$_{3}$ Films. K. Chu and J. P. Chang, Department of Chemical Engineering, University of California, Los Angeles, CA; M. Steinweg, H. M. Fleming, R. P. Ollis, D. V. Long, and C. D. W. Jones, Bell Labs, Lucent Technologies, Murray Hill, NJ.

Thermal, opto-electronic, and magnetic properties of a new class of amorphous materials, α-Fe$_2$O$_3$/α-Al$_2$O$_3$(001) films, have been studied using a variety of techniques, including X-ray reflectivity, X-ray photoelectron spectroscopy, and magnetization measurements. The films were grown on Si(001) substrates by reactive magnetron sputtering using a target composed of a mixture of α-Fe$_2$O$_3$ and α-Al$_2$O$_3$(001). The X-ray diffraction patterns of the films were indexed to a tetragonal crystal structure, and the magnetic properties were consistent with the tetragonal structure. The magnetic properties were found to be dominated by the α-Fe$_2$O$_3$ phase, and the α-Al$_2$O$_3$ phase was present in very small quantities. The films were magnetic and exhibited a Curie temperature of around 500 K. The magnetic properties were also found to be dependent on the growth conditions, and the films with the highest magnetic properties were grown at the highest growth temperatures.
400°C, resulting in the increase of surface roughness. Finally, the heteropercipitral misaligned grains start to nucleate directly on the oxide layer. A high temperature treatment was further performed by depth profile analysis using Auger Electron Spectroscopy. This work is supported by DARG-55-8H1-30012 and NSF-DMR-9801759 grants.

9:15 AM 09.4 EVOLUTION OF THE ELECTRO-OPTIC EFFECT WITH THE CRYSTALLINITY OF BARIUM TITANATE THIN FILMS
M. Siegenthaler, D.J. Werder, and H.Y. Hwang, Bell Laboratories, Lucent Technologies, Murray Hill, NJ

Ferroelectric oxide thin films are currently actively studied for a number of applications, including memory elements and electro-optic devices. A general issue is the dependence of the relevant physical properties on the length scale of crystallinity. We have studied a series of polycrystalline BaTiO3 thin films grown by pulsed laser deposition, where the crystalline coherence length is systematically varied from nanometer-sized grains to polycrystals by varying the deposition temperature. The structural properties have been studied by x-ray diffraction and transmission electron microscopy and compared with the evolution of various optical properties including the electro-optic effect.

9:30 AM 09.5 MICROSTRUCTURE EVOLUTION AND CRYSTALLISATION KINETICS OF SOLUTION DEPOSITED PLZT THIN FILMS
Mohammed El-Saadi, Andrés Picon, University of Applied Sciences, Surface and Thin Films Technologies, Kiel, GERMANY

The results of the microstructure development and crystallisation kinetics of solution deposited lead-zirconate-titanate (PZT) and lanthanum doped PZT (PLZT) on different electrode types including highly textured [111]Pt, polycrystalline Pt and a conductive transparent oxide are reported. It is shown that the crystallisation kinetics and the grain size depend strongly on both thin film composition and electrode type. Undoped PZT exhibits fastest kinetics on [111]Pt. The results are interpreted in terms of grain boundary nucleation and growth kinetics and are interpreted in terms of interfacial reactions and interfacial stresses between the thin film and substrate.

9:45 AM 09.6 THE SIZE EFFECT OF THE POLARIZABLE NPt

In recent years, the FeRAM integration technology is enough for manufacturing commercial products using the design rule from 0.8um to 0.3um. The FeRAM technology is improved toward to realize the next generation high density FeRAM on 0.18um sub-micron design rule. However, it is known that the ferroelectric characteristics changes between the bulk crystal state and the thin film state, fabricated for the high density FeRAM. Therefore, the theoretical chiralization of the high density FeRAM characteristic is become very important to realize the next generation FeRAM device on time. The size dependence of the polarization of NbTiO3 nanoscale NbOx (SBTN) ferroelectric capacitor was calculated in this work by classical capacitor model with the polarization normal to the electrodes. Two different mechanisms, the depolarization field and the surface effect due to the change of the long-range interaction between the polarization in the vicinity of the surface and interface, were mentioned theoretically to calculate the size effect of the polarization.

The free energy expression of the polarization is described as a function of position using the Landau theory with the boundary condition. The total polarization of the capacitor was described by the integration of the capacitance volume with the expression coefficient as a fitting parameter was calculated from the experiment data of the polarization. The simulations of the size dependence of the polarization were performed. The simulated results shows that the polarization is stable down to capacitor size 0.1um² and thickness 10nm. In conclusion, the ultra high density FeRAM using SBTN can be realized from the simulation of the size dependence of the polarization.

10:30 AM 09.7 HIGH RATE IN-SITU YBCO DEPOSITION: THERMODYNAMIC CONSIDERATIONS
Takeyoshi Okahashi, William Jo, Ann Marshall, Jessica Jen, Robert H. Thiemann, and M. H. Brodsky, University of Illinois, Laboratory for Advanced Materials, Stanford, CA; Eric Peterson, Los Alamos National Labs, Los Alamos, NM

We are developing a high rate (up to 10 nm/s), in-situ YBCO film synthesis using an electron beam deposition method with a view
toward coated superconducting conductors for electrical power applications. Different from YBCO films grown with low rate deposition techniques, the films have other unique microstructural properties. Inclusion of large bulk-like \( \gamma \)-\( \text{PbO} \) precipitates (\( \sim 100 \) nm), existence of surface nanocrystalline layer, and two kinds of YBCO layers with different crystallinity underneath it, leading to transmission electron microscopy (TEM) energy dispersive x-ray survey, Bi-\text{MeO}_2 etching, electrical transport measurements, and X-ray diffraction results. Former two features seem to indicate that the YBCO film is growing in Y deficient Bi-\text{Cu}_2O liquid flux, even though we are depositing only stoichiometric YBCO. The liquid layer is surprising considering our low oxygen pressure conditions, and we are attempting explain it based on the thermodynamics of activated oxygen in this system. By depositing a Y doped Bi-\text{Cu}_2O liquid layer before the stoichiometric YBCO layer, we are attempting grow only stoichiometric YBCO with high current density. Our LPE type of growth resembles Tri-phase epitaxy [1] but at order of magnitude lower pressure. The results of LPE, the liquid layer formation and decomposition YBCO film growth was discussed in the reflection high energy electron diffraction. [1] M. Kawasaki, D. B. Choi, T. Ito, K.S. Yun, and H. Kobayashi, *Proceedings of the third symposium on atomic scale surface and interface dynamics* 3, (1993) 151.

10:45 AM 09.8

**TAILORING MANGANESE PEROVSKITE SURFACES**

C.N. Bece, Bo Xu, Takashi Komessu, Hae-yung Jeong, M.T. Liu, S.A. Benner, P.A. Dowben, University of Nebraska, Department of Physics and Astronomy, Lincoln, NE.

We have studied the surface composition and electronic structure of CMR perovskite thin films of \( \text{La}_x \text{Sr}_y \text{Mn}_z \text{O}_3 \). Depending on the annealing treatments, the thin film surface exhibits widely different behavior and composition. A gentle annealed surface shows 88% spin symmetry close to Fermi level, at the surface Brillouin zone center, and a Curie temperature of 335 K, while a heavy annealed surface has a reduced polarization (45%) and a nonmetal-metal transition temperature of 245 K. The composition of the two types of surfaces was analyzed using angle dependent X-ray photoemission, and the unoccupied bands were assigned by comparing the X-ray absorption with inverse photoemission spectra. As expected, the high polarization near the Fermi level is a consequence of the Mn atoms, which contributed to the majority of the magnetic moment. Tailoring surfaces of complex CMR compounds may lead to improvements in device performance. The current results shed considerable light on the device performance of the CMR perovskites in tunnel magneto-resistive junctions and spin valves in the thin film limit.

11:00 AM 09.9

**EVOLUTION OF THE MICROSTRUCTURE, GROWTH STRESS AND STIFFNESS OF ALUMINA THIN FILMS DURING VAPOR DEPOSITION.**

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

The stress in alumina thin films, s-beam deposited on a silicon or sapphire substrate, was monitored in situ with measurements of the substrate curvature. At 400C, the growth stress is tensile, with a magnitude of 200 MPa for thicknesses up to 700 nm; at high thicknesses, the magnitude decreases. Interception of the deposition causes no change in the curvature. Thermal cycling up to 450C results in reversible curvature changes, due to thermal stresses. From these, the biaxial modulus and coefficient of thermal expansion of the films could be determined. The biaxial modulus decreases continuously with thickness, from a value of 310 GPa at 100 nm to 65 GPa at 2000 nm. This decrease correlates with a decrease in density, on the order of 15%. The increased porosity is accompanied by increased surface roughness, observed directly by AFM and SEM, as well as by interferometry on the reflections of the curvature measurement. A quantitative model for the relation between thickness, density, stiffness and growth stress is being developed.

11:15 AM 09.10

**PHASE FIELD MODELING OF ELECTRODEPOSITION**

J.E. Geyer, W.J. Boettger, and J.A. Warren Metallurgy Division, National Institute of Standards and Technology, Gaithersburg, MD.

We will present a novel computational model of electrophotography, using the phase field method. The phase field method models the macroscopic solute and interfaces of a sharp (two dimensional) transition between liquid and solid. This sharp transition requires tracking of the position and shape of the liquid-solid interface and the application of boundary conditions at the solution-solid interface. The computational difficulty of this task is for all but the simplest geometries. Phase field calculation, on the other hand, defines a variable and a corresponding governing equation to describe whether a material is solid or liquid as a function of both position and time. With the addition of conventional diffusion equations, the evolution of complex growth patterns and the equations for the dynamics of the process can be solved without tracking the liquid-solid interface. The numerical method is a finite difference mesh, making implementation straightforward for the novice programmer. This method allows us to treat the complex geometry, including void formation, that occurs during plating in vats and trenches for on-chip metallization. It also provides for a proper treatment of curvature effects on the overpotential. The phase field technique has been successfully applied to such complex morphologies as the cellular breakdown of high-velocity directional solidification and dendrite formation under convective flow, but this is the first time that phase field modeling has been applied to electrochemical problems. This work was motivated by the mathematical analogy between the governing equations of solidification dynamics and electroplating dynamics but it is not surprising that we find significant differences between the two systems. Indeed, the inherent non-linear kinetics in electrodeposition is far different from solidification, where problems are generally well-modeled with linear kinetics. We will present different techniques for deriving these non-linear phase field equations and the consequences of each.

11:30 AM 09.11

**GROWTH AND CRYSTALLOGRAPHIC ORIENTATION OF ELECTROMIGRATION-INDUCED HILLOCKS IN ALUMINUM INTERCONNECTS.**

J.A. Nucci, C.A. Volkert, A. Strasz and E. Arzt, Max Planck Institute for Metals Research, Stuttgart, GERMANY.

Hilllocks form in metal films due to compressive stress generated either by thermal cycling or electromigration. Understanding how they grow may help to elucidate possible mechanisms for atomic motion and stress relief in thin films. In this study we have carefully investigated the morphology and crystallography of electromigration-induced hilllocks, from which their growth mechanism can be determined. Hilllocks consisting of columnar, AlII segments of various lengths and connected by a continuous underlying Ni layer were electromigration tested at 250°C and 1 mA/m². After two hour intervals, the test was interrupted and hillock orientations were investigated using electron backscattering diffraction. Finally, the microstructure of the hilllocks was extensively characterized using atomic force microscopy, field emission SEM, TEM, and focused ion beam (FIB) microscopy. FIB cross sections revealed that hilllock growth occurred by planar addition of Al atoms at the Al/Ni interface. As the hilllocks grew, their normal directions rotated away from [1 1 1] texture accompanied by rigid body rotation of the entire grain about the same axis, as determined from the surface morphology. Such growth is consistent with atomic diffusion along grain boundaries and down into the bottom interface, which pushes up and rotates the hilllock as it grows.

11:45 AM 09.12

**SESSION 010: SILICIDES AND ORGANIC THIN FILMS**

**PULSED LASER DEPOSITION**

Chair: Jacques G. Amar and John E. Sanchez, Friday Afternoon, April 20, 2001

*Salon 7 (Marriott)*

**1:30 PM 010.1**

**SELF-ASSEMBLED SILICIDE NANOWIRES GROWN ON SILICON**

Yong Chen, Douglas A.A. Oldberg, R. Stanley Williams, Hewlett-Packard Laboratories, Palo Alto, CA.

Many silicides have a symmetric lattice-mismatch to Si(001) host substrate, which can break the growth symmetry and lead to the self-assembled epitaxial growth of silicide nanowires. Four silicides, ScSi, ErSi, DySi, and GdSi with different lattice-mismatches have been chosen to grow on Si(001). The widths and the lengths of the nanowires were in the range of 3-15 nm and \( \sim 100-1000 \) nm, respectively, for different lattice-mISMATCHES and growth conditions. The larger lattice-mismatches along the width direction led to the narrower wires, and the smaller lattice-mismatches along the length direction led to the longer lengths. This method provides an effective way to fabricate one-dimensional quantum system with desired sizes for novel physical properties.

**1:45 PM 010.2**

**LOW TEMPERATURE HETEROPITAXIAL TITANIUM SILICIDE PHASES IN 3 nm ISLANDS SEEN ON \( \gamma (7 x 7) \)**

**TITANIUM PHASES AT T \( \sim 500\)°C.**

N. Herbert, J.M. Shan, M. Liger, M.P. Grimes, D.J. Smith, Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ.

3-nm wide titanium silicide islands are formed on \( \gamma (7 x 7) \).
templates below 500 degree Celsius by Combined Ion and Molecular Beam Deposition (MBD) in order to investigate the possibility of obtaining a continuous titanium silicide film by the deposition of 28.8 nm [7x7] unit cells. These temperatures are compatible with quantum dot processing, by minimizing surface diffusion. After growth room temperature deposition of Si, followed by low temperature deposition of rapid thermal oxidation is used to further isolate and encapsulate the dots to protect them from oxidation in air for electrical measurements while working on the NSF seed. Indeed, if exposed to air without encapsulation, the dots tend to vanish. Two distinct colors of titanium silicide dots are achieved below 800 K. The first silicide phase formed is found to be close but not lattice matched to Si[111] by RHEED diffraction. Plan-view HRTEM shows that this grain phase consists of the characteristic triangular shape of a periodic island nucleation [7x7][Si111] unit cell. The second silicide phase has about twice the lattice constant of Si[111] and facets in a more complex polygonal shape. Interference fringes in HRTEM imaging is observed within the two kinds of islands confirms the RHEED findings. Our current understanding is that the second silicide phase appears to be close the C54 titanium disilicide phase along the c-axis. Results from Electrical measurements, high resolution Medium Energy Ion Scattering (MEIS) combined with Channeling and Blocking and Atomic Force Microscopy results will also be discussed. Support by the National Science Foundation under grant DMR-93263 is hereby acknowledged.

2:00 PM 10.3

DYNAMICS OF SHAPE TRANSITION OF EPITAXIAL TiSi2 ISLANDS ON Si[111] SURFACES. Wookchul Yang, R.J. Nemaniich, North Carolina State Univ, Dep of Physics, Raleigh, NC.

The evolution dynamics of the shape and size of nanoscale TiSi2 islands on Si[111] surfaces is explored using a novel epi-silicon photoluminescence microscopy (UV-PEEM) in situ continuous deposition at elevated temperature and real-time microscopy of the growth of the islands can allow us to study the competitive shape evolution of the individual islands. The islands were prepared by in situ Ti deposition of -<100> at room temperature followed by annealing to 1550°C. During annealing, we observed island coarsening (both ripening and coalescence) where smaller islands evolved into larger islands and the surface morphology displayed a dilute island distribution. In addition, high temperature deposition of Ti for further growth of the islands led to increased size of islands and real-time monitoring of the growth of the islands can allow us to study the competitive shape evolution of the individual islands. The islands were prepared by in situ Ti deposition of -<100> at room temperature followed by annealing to 1550°C. During annealing, we observed island coarsening (both ripening and coalescence) where smaller islands evolved into larger islands and the surface morphology displayed a dilute island distribution. In addition, high temperature deposition of Ti for further growth of the islands led to increased size of islands and real-time monitoring of the growth of the islands can allow us to study the competitive shape evolution of the individual islands.

2:15 PM 10.4

INFLUENCE OF DENDRIMER INTERLAYER ON METAL ADSORPTION. A. Rar, G. Wei, F.T. Xu, J.A. Barnard, The Center for Materials for Information Technology, M. Curry, S.C. Street, Department of Chemistry, The University of Alabama, Tuscaloosa, AL.

Si wafers covered with a native oxide were used as substrates for the growth of thin metal layers, mediated by a self-assembled monolayer of amino-terminated poly[methoxylamine] (PAMAM) dendrimers (generation G) 4, 8 and 10. The films were studied using a combination of XPS, XRR (x-ray reflectivity), AFM, and nanindentation. It was shown recently [1], that for an inert metal, such as Au, metal atoms penetrate into G dendrimer, leading to improvements in film quality. When dendrimers are used as an interlayer, the film is enhanced. The surface roughness decreased by three-fold, and better adhesion was noted. Penetration should be less pronounced for active metals such as Al, Co, Cr and Cu, because of increased chemical activity with the outermost amine terminal groups. The outer shell of the dendrimers become more dense with increasing generation number, thus penetration of the deposited metals should follow the trend G4 > G8 > G10. This is confirmed by XPS, and related to observed mechanical properties and morphology of the deposited films. Apparently, for the more active metal, a bilayer system gives a mechanically softer film as a result of yielding of the dendrimer interlayer during nanindentation. 1. A. Rar, J.N. Zhou, A. Bennett, W.J. Liu, J. Barnard, and S.C. Street, Dendrimer - Mediated Growth: Very Thin Utrahin Au Films. Appl. Surf. Sci., in press.

2:30 PM 10.5

INVESTIGATION OF MATERIAL FLOW ON INSULATING A POLYMER SURFACE GRATING PROBING X-RAY AND VIS LIGHT SCATTERING. Thomas M. Genre, Oliver Henneberg, Marin Sapmaz, Ulrich Fiechter, University of Potsdam, Institute of Physics, Potsdam, GERMANY; Almirante Nautical, Queen’s University, Department of Chemistry, Kingston, ON, CANADA; Paul Rochon, Royal Military College, Department of Physics, Kingston, ON, CANADA; Ken Finkelnburg, Cornell University, CHESS, Ithaca, NY.

Surface relief patterning on amorphous polymer films containing azobenzene-side chains can be performed by holographic exposure with phase-shifting masks at room temperature below 808 nm. The film under investigation were made from a series of polyazobenzene side-chain homopolymers. The efficiency of grating formation is probed by the time development of the diffracted first-order grating peaks intensities. While the VIS signal increases over time, the intensity of the Bragg intensity increases very slowly. As the holographic exposure, the x-ray grating peak intensity reaches a maximum after about 60 s and decreases thereafter. Similar measurements during short time exposure show that the maximum of the x-ray signals depend almost the entire pulse length of the inscribing light. An analysis of the time evolution of the VIS scattering reveals the existence of sequential elastic and plastic processes during exposure. Both experiments can be explained qualitatively by assuming the formation of a density grating in addition to the surface relief patterning. Our assumption is validated by model calculations using a finite element (FE) approach including a viscoelastic force distribution accompanied by viscoelastic flow.

2:45 PM 10.6

VERTICAL LAMELLAE IN THE CMOS OF DIPOLE COATTERMETERS. Delee-M. Szeles, Cornell Univ, CHESS, Ithaca, NY; Christine Papadakis, Peter Bash, Univ of Leicrab, Dept of Physics and Geosciences, Leipzig, GERMANY; Dorthe Posselt, Roskilde Univ., Dept of Mathematics and Physics, Roskilde, DENMARK.

Polymer coatings have great technological importance for e.g. integrating circuits and optical coatings. Hence investigations of the microstructure of polymer blends and stock components has become an important field of research in recent years. Recently we have found that symmetric di-block polymer of poly(styrene-polybutane) prepared by spin-coating onto Si-wafers can form lamellae oriented perpendicular to the substrate surface, provided the molecular weight of the polymer is above 92 kg/mol. Polymer having molar masses below 22 kg/mol form the well known horizontal lamellae parallel to the surface. We have studied such films using a combination of atomic force microscopy (AFM) as well as synchrontron based x-ray reflectivity (XR) and grazing-incidence small angle scattering (GISAXS). Our AFM studies were invaluable for the optimization of sample preparation procedures. However, the internal structure of the films is not accessible to this probe. Hence we complemented our studies with x-ray scattering techniques, XR to probe the normal density correlations in the film, and GISAXS to probe the internal structure of the film. In order to enhance the scattering contrast, the butadiene blocks were stained with uranium tetrioxide. We studied such films at various thicknesses and molar weights. Films with molar masses between 92 to 183 kg/mol show XR and GISAXS scattering indicative of the lamellae containing all the way from the surface to the substrate. Most interestingly we found that films of intermediate molar weights in the range of 55 to 70 kg/mol. The AFM pictures show an inhomogeneous surface with some onion-like regions of vertical lamellae inbetween unstructured areas. Consistent with this finding, XR and GISAXS indicate a fraction of parallel lamellae and a curve of the vertical lamellae, respectively. Hence, using a combination of AFM, XR, and GISAXS a full characterization of the microstructure of polymer thin films can be achieved.
is found to be independent of the incoming flux of the metal atoms ejected from the PLD target. Slowing the moving metal atoms by helium tenor delays the onset of perovskization. In contrast, growing the metal films on atomically flat surface such as sulfur or MgO favors the early onset of the perovskization. Under favorable conditions, PLD Cu or Au films as thin as 1.5 nm would perovskize, and the threshold is at least a factor of 3 better than evaporated thin films. At about 5 nm, the conductivity would reach 30% of the bulk value. It is expected that by controlling various PLD parameters, the optical and electrical properties of semiconducting metal films can be engineered. The fabrication of these metal films is also under investigation. [1] S.K. So, H.H. Rong, C.F. Yeung, and N.H. Cheung, Appl. Phys. Lett. 77, 1099 (2000).

3:45 PM O10.8
PULSED LASER DEPOSITION OF DENSE PEROVSKITE FILMS ON MACROPOROUS SUBSTRATES FOR GAS SEPARATION APPLICATIONS
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Pulsed-laser deposition (PLD) was investigated for depositing thin films of the mixed ionic-electronic conducting perovskite La1-xSrxCoxO3 (LSO) on macroporous α-Al2O3 substrates (pore size ~100 nm) for use as oxygen separation membranes. It is demonstrated that reduced oxygen pressure deposition at room temperature leads to smooth, uniform and dense films that are completely gas-tight to nitrogen gas whereas films deposited at high oxygen pressures are rough, granular and porous. Moreover, we report on the deposition of LSO films on macro-porous LSC substrates (pore size > 1 µm) in an attempt to develop all-perovskite oxygen separation membranes. Prior to the deposition, the substrate surfaces were chemically etched or modified with a dip-coating. It is found that, under the right deposition conditions, continuous and non-porous films with excellent textures can be grown on these types of substrates. First oxygen permeation measurements reveal that the films show very high oxygen fluxes at temperatures between 700 and 1000 degree Celsius.

4:00 PM O10.9
HETEROEPITAXIAL GROWTH OF TAN ON MgO(001) AND TiN(001)/Si(001) BY PULSED LASER DEPOSITION
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Epitaxial TaN[001] films have been successfully grown on MgO[001] single crystal and TiN[001]/Si[001] buffered Si[001] substrates by pulsed laser deposition method. Crystalline TaN layers of about 100 nm thick were deposited under a base pressure of 5 x 10^-6 Torr and at substrate temperatures ranging from 500°C to 700°C. X-ray diffraction results suggested that stoichiometric TaN films with cube-on-cube (001)PbCO3(001) heteroepitaxy are obtained in this temperature range. Plan-view and cross-sectional electron microscopy analysis revealed excellent structural quality and sharp interface boundary. TaN films grown on TiN[001] buffer Si[001], however, showed a mixture of TaN2 (with x ~ 1) components. Although the (001)TiN oriented TaN is always present prominently, the nitrogen deficient TaN2, components are often co-exist in the films and show up as a very broad peak in the X-ray diffraction profile. Their magnitude and position change with the deposition temperature and show a strong dependence on the growth condition of the TiN buffer layers. Stoichiometric and single phase TaN[001] films can only be obtained in a narrow temperature window of around 550°C and heteroepitaxial relation (001)TaN//(001)PbCO3, has been demonstrated.

4:15 PM O10.10
SYNTHESIS OF TIN OXIDE THIN FILMS BY PULSED LASER DEPOSITION
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Tin Oxide (SnO2) has been utilized as a gas sensing material, because it shows an electric conductivity change in contact with flammable gases. SnO2 thin films have been grown on Si[100] and Al2O3 substrates by pulsed Nd:YAG (532nm) and KrF excimer (318 nm) laser deposition method using SnO2 targets. The effects of substrate temperature and oxygen gas pressure on the properties of the SnO2 thin films are discussed. Surface morphology and structure of the films have been obtained by field emission scanning electron microscopy (FE-SEM), x-ray diffraction (XRD) and glancing angle x-ray diffraction (GXRd) measurement. GXRd showed that, with increasing oxygen gas pressure, the almost amorphous microstructure transformed into a crystalline SnO2 phase and preferred orientations varied from [110] to [111] on Si[100]. This result suggests that oxygen gas pressure affects the phase formation, crystallline and preferred orientation of the films. Gas sensing properties of SnO2 thin films by PLD method are also investigated over the temperature range 423K - 873K, using H2 or CH4 as test gases.

4:30 PM O10.11
Pb(Mg1/3Nb2/3)O3-Pt/TiO2 RELAXOR THIN FILMS BY PULSED LASER DEPOSITION
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The relaxor composition (Pb(Mg1/3Nb2/3)O3)0.95(Pt/TiO2)0.05 thin films were deposited by PLD on Pt/TiO2/ SrO/Si substrates. Several growth parameters were varied to optimize the film properties, which include: substrate temperature, sputter oxygen pressure, laser fluence and the annealing temperature. Pure perovskite phase in polycrystalline thin films grown at different substrate temperatures (300 - 650°C) were obtained after the films were subjected to an annealing at 580°C. Films were characterized in terms of structure (XRD), phase identification (micro-Raman), morphological properties (AFM) and electrical behavior. Films with near complete perovskite phase exhibited a dielectric constant of about 2500 and a dissipation factor of about 0.02. Detailed results on structural and electrical studies will be discussed in close correlation with the processing conditions.

4:45 PM O10.12
PULSED-LASER DEPOSITION OF TiN SHAPE MEMORY ALLOY THIN FILMS AT DIFFERENT TEMPERATURES

Thin films of TiNi shape memory alloy (SMA) have been prepared by pulsed-laser deposition (PLD) at different substrate temperatures. The stoichiometry, deposition rate, and crystallinity of the deposited films were characterized by X-ray photoelectron spectroscopy (XPS), surface profile measurements, and X-ray diffraction (XRD). The transformation behavior and crystallization temperatures were investigated by differential scanning calorimetry (DSC). It is found that the deposition rate vary with the order of 1.2 nm per pulse. The Ni content range from 46.7 to 52.9 at.%. The film deposited at a substrate temperature of 600°C has a polycrystalline structure and austenite is the major phase. The martensitic transformation temperature the measured 51.5 ±5%. Ni thin film is determined to be ~208°C. The crystallization temperatures of the amorphous films are around 430°C. It can be concluded that the substrate temperature plays an important role in the composition control and the crystallization of the films.