

SYMPOSIUM L

Recent Developments in Oxide and Metal Epitaxy— Theory and Experiment

April 23 – 26, 2000

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* Invited paper

TUTORIAL

ST L: IN SITU CHARACTERIZATION TECHNIQUES FOR THIN FILM EPITAXY

Sunday, April 23, 2000
1:30 p.m. - 5:00 p.m.
Golden Gate A3 (Marriott)

Thin film epitaxy is integral to many current and emerging technologies and continued progress in solving fundamental issues is critical. In-situ characterization techniques are receiving increasing attention since they offer the possibility to reduce the often unavoidably empirical nature of thin film research and enhance efficiency significantly. Techniques to be covered in the tutorial probe surface and buried interface processes in thin film epitaxy. They include in-situ electron-beam characterization of complex-oxide MBE, integrated in-situ time-of-flight ion scattering and recoil spectroscopy, in-situ spectroscopic ellipsometry, x-ray photoelectron spectroscopy and auger electron spectroscopy.

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SESSION L1: GROWTH AND DYNAMICS OF METAL FILMS

Chairs: Shirley Chiang and Andreas K. Schmid
Monday Morning, April 24, 2000
Salon 10/11 (Marriott)

8:30 AM *L1.1

TAILORING EPITAXIAL TEMPLATES FROM REFRACTORY
METAL BUFFERS. C.P. Flynn, University of Illinois, Urbana, IL.

Refractory bcc metals buffer sapphire from reactive epilayers and offer a variety of template symmetries for epitaxial crystals. The variety of valuable thin film systems grown by molecular beam epitaxy using these methods include rare earth metals and alloys in several orientations, intermetallic compounds such as Cu_3Au and stricture magnets like TbFe_2 . Six distinct orientations to Ti can be selected by choice of orientation and buffer. We have discovered that Nb (011) single crystal buffers, as deposited on sapphire (11 -20) develop surface mesostructures whose boundaries take the form of {110} facets [1]. The evolution of these features depends on growth temperature, film thickness and vicinal miscut. When used as templates for subsequent growth of fcc noble metals, the mesostructures control nucleation and may be employed to select stacking and eliminate twins. We have examined $\text{L}_{12} \text{Cu}_3\text{Au}$ grown (111) on Nb (011) buffers as a function of vicinal miscut [2]. From symmetry the stacking twins ABCA.. and ACBA.. occur equally on Nb (011). We find that a 1° miscut along [100] suffices to eliminate all but 0.1% of the less favored twin. The control offered by these templates has led us to examine the evolution during annealing of Nb (011) surfaces grown on sapphire, using low energy electron microscopy (LEEM), at temperatures up to 1700K. For vicinal miscuts of about 0.1° we directly observe the coalescence of step edges into {110} nanofacets [3], creating broad, relatively perfect terraces up to many microns in extent [4]. The behavior differs for [100] and [0 -11] miscut, and a tentative phase diagram for nanofacetting is proposed. Slip traces, dislocation glide and the interaction of slip with surface steps can all be clearly imaged. The short term goal is to grow epilayers on tailored buffers in the LEEM, and to observe and optimize the controlled nucleation processes directly.

- [1] G.L. Zhou and C.P. Flynn, Phys Rev B59, 7860 (1999)
- [2] S.W. Bonham and C.P. Flynn Phys Rev B58,10875 (1998)
- [3] C.P. Flynn and W. Swiech, Phys Rev Lett 83, 3482 (1999)
- [4] W. Swiech, M. Mundschau and C.P. Flynn, Surf Rev Lett 5, 1221 (1999)

9:00 AM *L1.2

COMPLEX TEMPERATURE DEPENDENCE OF Ag/Ag(100)
MULTILAYER GROWTH. C.R. Stoldt, K.J. Caspersen, T. Layson,
M.C. Bartelt, J.W. Evans, P.A. Thiel, Iowa State University, Ames,
IA.

Metal(100) homoepitaxy constitutes the simplest example of multilayer film growth, and is thus a natural testing ground for ideas on kinetic roughening. Surprisingly, from VT-STM studies of 25ML Ag/Ag(100) films grown between 50K and 300K, we find a variation of roughness, W, with temperature, T, more exotic than any observed previously in metal epitaxy! Non-monotonic variation of W with T has been observed, e.g., for Pt/Pt(111) and Rh/Rh(111) growth, but

it was tied to a dramatic change in 2D island morphology. For Ag/Ag(100), there is no such morphological change. Yet, while W at first increases classically due to inhibited downward transport as T decreases from 300K to 220K, it then decreases below 220K achieving a minimum at about 140K, and finally actually increases again for lower T. Detailed atomistic modeling and simulations suggests the following interpretation: the increase from 300K to 220K reflects more restricted downward transport due to a small step-edge barrier; the decrease from 220K to 140K reflects enhanced downward funneling from the more prevalent step edges [1]; the increase below 140K reflects a breakdown of downward funneling at small, steep micro-protrusions on the surface. We also characterize the T-dependence of other features of the film morphology (mound densities and slopes), and quantify up to 100ML the most rapid kinetic roughening which occurs around 220K.

[1] M.C. Bartelt and J.W. Evans, Surf. Sci. **423** (1999) 189; Phys. Rev. Lett. **75** (1995) 4250.

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9:30 AM L1.3

LATTICE MODEL FOR GRAIN BOUNDARY DE-FACETING
TRANSITIONS OBSERVED IN THIN FILMS. John C. Hamilton,
István Daruka, Sandia National Laboratories, Livermore, CA.

The motion of grain boundaries plays a critical role in determining the properties of thin films especially during use at temperature. In spite of this fact, the motion of grain boundaries is not well understood. A classic experiment by Hsieh and Balluffi* shows a reversible de-faceting transition of incoherent twin boundaries in an aluminum thin film at about 400K. Below this temperature large facets are seen; above this temperature the grain boundary becomes smooth at the length scale of observation. We initially modeled this transition using molecular dynamics. We learned that the grain boundary could move only at junctions between two facets. This motion occurs by a cooperative motion of four atoms at the junction. Such an excitation transforms one primitive cell of the coincidence site lattice from one grain orientation to the other thereby moving a portion of the grain boundary. This elementary excitation was mapped onto a simple two-dimensional lattice model incorporating both the topology of the boundary and the energy associated with the excitation. With the lattice model, large-scale simulations of the de-faceting transition were performed. The grain boundary structures calculated from the lattice model were in excellent agreement with the molecular dynamics calculations and with the experimental observations. By examining the roughness, the disorder, and the specific heat as a function of temperature, we were able to prove that the de-faceting transition is in fact a phase transition and to determine the order of this transition. The lattice model described here is applicable to studies of grain coarsening, and grain mobility in other thin film systems. * T.E. Hsieh and R.W. Balluffi, Observations of Roughening/De-faceting Phase Transitions in Grain Boundaries, Acta metall. Vol. 37, 2133 (1989).

9:45 AM L1.4

REAL TIME OBSERVATION AND QUANTIFICATION OF
DISLOCATION MEDIATED PLASTICITY IN BICRYSTAL Al (011)
on Si (100). E.A. Stach and U. Dahmen, National Center for Electron
Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA;
W.D. Nix, J. Florando and O. Leung, Department of Materials
Science and Engineering, Stanford University, Stanford, CA; A.
Schwartzman, Department of Materials Science and Engineering,
Brown University, Providence, RI.

The mechanical properties of thin metallic films on silicon have been a topic of intense study over the past several decades. Various mechanical testing techniques - including wafer curvature, nanoindentation and microbeam bending - have been developed to elucidate the mechanisms by which strains are relaxed during thermal cycling of these structures. In this work, we focus on the strain relaxation behavior of a model heteroepitaxial metal film / silicon substrate system. Deposition of aluminum onto silicon at a substrate temperature of 280°C results in the formation of a mazed bicrystal structure consisting of two variants of Al (011) (Tharangaj, et al., APL, 1992). By subjecting these structures to thermal cycles within the electron lens of a transmission electron microscope, we are able to observe directly the nucleation and motion of dislocations within the aluminum grains via diffraction contrast imaging. Upon cooling from an annealing temperature of 450°C, we find that pre-existing dislocations initially move slowly, within the plane of the film, by a combination of stress-assisted dislocation climb and cross-slip. This results in little relaxation of strain. At the tensile yield point, however, dislocation nucleation and glide is observed to occur along the four {111} $1/2 < 110 >$ slip systems in a dramatic burst. Subsequent dislocation motion upon further cooling is strongly hindered by dislocation - dislocation interactions. The simplicity of the crystal microstructure in these films permits direct correlation of our observations of dislocation motion with quantitative

measurements of epilayer strain and theoretical models of dislocation behavior. We will compare and contrast our observations in these model bicrystal aluminum samples with similar observations we have made in large-grained polycrystalline samples, thereby shedding light on the mechanisms by which dislocations mediate plasticity in metal films on silicon.

10:30 AM *L1.5
SPATIAL CORRELATIONS IN GROWING FILMS. M.C. Bartelt, Sandia National Laboratories, Livermore, CA.

Detailed analyses of non-equilibrium lattice-gas models of island nucleation and growth during film deposition or etching have been invaluable in elucidating basic issues in nucleation theory, deviations from mean-field predictions, and experimental observations. Particularly interesting and useful is the behavior of correlations in the adlayer which develop during island formation. Spatial non-uniformities in the density, n , of diffusing adspecies determine island nucleation positions. In particular, a strong depletion in the population of island pairs at separations smaller than the average follows from depletion in n near islands. This feature delays island percolation. In addition, island-free areas surrounding islands are larger for bigger islands, reflecting strong correlations between island size and separation. Through the island size dependence of the island capture numbers, these correlations control the shape of the island size distribution [1]. When incorporated into rate-equation descriptions, they recover the exact form of the scaling function for the island size distribution [1,2], thus overcoming long-standing limitations of traditional mean-field treatments. I will illustrate several of these features with results from epitaxy and etching studies [2]. For example, for Co islands on Ru(0001), I show how the rate and direction dependence of capture of additionally deposited Cu atoms reflect the local environment of individual islands, as predicted by simulation and diffusion-equation analyses. Similar observations were reported on the growth of etch pits on Si(100) monitored with LEEM during exposure to oxygen. Here, I also compare actual pit nucleation positions with predictions from simulations and a diffusion-equation analysis. Spatial correlations in the adlayer depend crucially on these initial stages of island nucleation. This work was supported by the USDOE-OBES under contract no. DE-AC04-94AL85000. [1] M.C. Bartelt and J.W. Evans, PRB54 (1996) R17359. [2] M.C. Bartelt et al., PRL81 (1998) 1901 & 4676; PRB59 (1999) 3125.

11:00 AM L1.6
RATE EQUATIONS AND EFFECTIVE CAPTURE NUMBERS. F. Gibou, C. Ratsch, UCLA, Dept of Mathematics and HRL Laboratories, Malibu, CA; S. Chen, R. Cafilisch, UCLA, Dept of Mathematics; M. Gyure, HRL Laboratories, Malibu, CA.

Mean field rate equations that form the basis of nucleation theory have been used for over 25 years to study epitaxial growth. One problem in using rate equations is that the functional form of the capture coefficients σ_S for islands of size S is not known. Several approximations for σ_S are given in the literature; while some correctly reproduce averaged quantities, none of these approaches has given the experimentally observed scaling of the island size distribution. In this paper, we show that the problem is the correct interpretation of the meaning of the capture numbers. We propose a new definition for these coefficients and compute them numerically using the level-set formalism. The main idea is that σ_S depends on the capture efficiency of all islands of sizes smaller than S . We then show for the first time that integration of rate equations gives the correct scaling of the island size distribution.

11:15 AM L1.7
FILM RIPENING BY RANDOM EXCHANGE OF ADATOMS. S.J. Koh, G. Ehrlich, Univ of Illinois at Urbana-Champaign, Materials Research Laboratory and Dept of Materials Science and Engineering, Urbana, IL.

In the later stages of overlayer growth on a surface, larger islands may grow at the expense of smaller islands, in a process known as Ostwald Ripening. The driving force for this is the higher chemical potential of smaller islands, which produces higher adatom concentrations and results in a net flow of adatoms from smaller to larger islands. Here, we wish to report that ripening can also occur by a random exchange of adatoms between surface clusters, without any chemical potential difference. This phenomenon has been observed in a model system: one-dimensional clusters of Ir on W(110). Two parallel one-dimensional Ir chains are prepared on the W(110) surface, which is then heated at 465K. The fate of individual atoms in the two Ir clusters is monitored with a field ion microscope. The length of each chain is observed to fluctuate as adatoms are exchanged between the two chains. Occasionally the smaller chain is found to grow, consuming the larger one. Detailed analysis shows that the exchange of adatoms between two chains is a random process. Analogous events are expected to contribute to the usual Ostwald Ripening, especially

when the difference in the chemical potential of participating particles is small. (Supported by the US Department of Energy under Grant No. DEFG02-96ER-45439)

11:30 AM L1.8
MODELING OF METAL (100) HOMEPIITAXIAL FILM GROWTH AT VERY LOW TEMPERATURES. K.J. Caspersen, C.R. Stoldt, P.A. Thiel and J.W. Evans, Iowa State University, Ames, IA.

In late 1980's, unexpectedly smooth growth was observed in metal(100) homoepitaxy around 100K, where terrace diffusion is inoperative. After some initial speculation on the role of transient mobility, this smooth growth was finally attributed to downward funneling of atoms deposited at step edges to lower four-fold hollow adsorption sites. Recent VT-STM studies for Ag/Ag(100) reveal rougher growth for even lower temperatures around 50K. Motivated in part by recent MD studies, we propose that the latter is due to restricted downward funneling where deposited atoms get caught on the sides of nanoprotusions. Above 50K, certain low-barrier thermal processes are also operative producing the observed additional smoothing by 100K. A lattice-gas model incorporating these features is shown to reproduce qualitatively experimental observations. Finally, we comment on a generic STM issue. For these low temperatures, where the film surface has small, steep nanoprotusions, one expects that the tip can not fully probe the surface, and thus produces a mollified morphology. We also discuss some consequences of this effect for a detailed comparison of experimental and simulated morphologies.

11:45 AM L1.9
THE LEVEL-SET METHOD FOR MODELING EPITAXIAL GROWTH. C. Ratsch and M.F. Gyure, HRL Laboratories, Malibu, CA; R. Cafilisch, S. Chen, M. Kang, B. Merriman, S. Osher and M. Wheeler, UCLA, Los Angeles, CA; D.D. Vvedensky, Imperial College, London, UNITED KINGDOM.

We develop an island dynamics model that employs the level-set technique to describe epitaxial growth. The surface morphology is described by defining the island boundaries as the set $\varphi = 0$ of the so-called level-set function. Islands are nucleated on the surface and their boundaries are moved at rates that are determined by the adatom density, which is obtained from solving the diffusion equation. Scaled island size distributions in the submonolayer aggregation regime are compared with those obtained from a kinetic Monte Carlo (KMC) simulation for irreversible as well as reversible aggregation. Excellent agreement is obtained. We identify spatial fluctuations in the seeding of islands as the only essential source of noise. We also show that the level-set method can naturally be extended to multilayer growth; here, the set $\varphi = n - 1$ corresponds to the n th layer. Roughening and Coarsening of the surface will be discussed. In particular, we will study the evolution of the step edge density, which is related to the RHEED signal in experiment. A qualitative and quantitative comparison to KMC simulations will be given.

SESSION L2: STRUCTURE AND OXIDATION OF METAL FILMS AND SURFACES
Chairs: Robin F. C. Farrow and C. Peter Flynn
Monday Afternoon, April 24, 2000
Salon 10/11 (Marriott)

1:30 PM L2.1
THE EFFECT OF DEPOSITION PRESSURE ON ADSORBATE STRUCTURE AND COVERAGE: OXYGEN ON W(110). D.E. Muzzall¹, C.S. Fadley^{1,2} and S. Chiang¹. ¹Dept. of Physics, University of California, Davis, CA, ²Materials Science Division and Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA.

In most prior surface science studies, it has been assumed that total exposure, rather than both pressure and time as independent variables, controls the types of adsorption structures formed. However, the potential importance of deposition pressure has recently been suggested in a study of the kinetics of the low pressure adsorption of oxygen on W(110) using photoelectron spectroscopy and diffraction¹. We have used ultrahigh vacuum scanning tunneling microscopy (STM) to explore the adsorbate structures and the coverage dependence of oxygen on W(110) as a function of the deposition pressure and for room temperature exposures. For the same total adsorbate exposure in Langmuirs (L), our study shows that changes in deposition pressure of as little as a factor of 3 cause significant changes in the apparent structures, domain sizes (e.g. of (1x2)O), and the actual resulting coverages of the adsorbate layer in monolayers. Low pressure deposition (3×10^{-9} torr) for total exposures of 2-12 L yields structures which do not show a distinct LEED pattern, but show small domains, approximately $20 \times 30 \text{ \AA}$, of local (1x2) ordering in the STM images. Total coverages measured directly from the STM

images vary only from 13-17% of a monolayer (ML) for this exposure range. In comparison, STM images of the surface resulting from intermediate pressure deposition (10^{-8} torr) show apparent domain sizes of approximately $30 \times 50 \text{ \AA}$ with adsorbate coverages of 15-30% ML. Higher pressure deposition (10^{-7} torr) for total exposures of 3 to 6 L yields structures with the well-known LEED patterns (1×2) and (2×2), and the STM images of these structures clearly show large well-ordered domains of these different types. The possible kinetic mechanisms of the adsorption leading to this strong pressure dependence will be discussed. Additional experiments to include the temperature dependence of these kinetic processes are in progress.

1. R.X. Ynzunza et al, Surface Science, in press.

1:45 PM *L2.2

HETEROEPITAXY: THE MISSING LINK BETWEEN SURFACE CHEMISTRY AND DRY CORROSION. Judith Yang, University of Pittsburgh, Dept of Materials Science and Engineering, Pittsburgh, PA.

Understanding the oxidation process is of fundamental and practical interest because thin film growth, such as ferroelectrics, corrosion, passivation, and some catalysis involve oxidation. However, there exists a surprising paucity of information concerning the transient oxidation stages, from the formation of the initial oxide to the growth of the thermodynamically-stable oxide. To bridge this gap, we are visualizing the initial oxidation of Cu(001) by in situ ultra-high vacuum(UHV) transmission electron microscopy (TEM). Oxidation potentially involves surface diffusion, nucleation and growth, which is strikingly similar to epitaxial deposition. We wish to apply and extend these theories of heteroepitaxy to explain the initial oxidation stage of a model metal system. The nucleation and growth of Cu_2O due to oxidation of Cu films were monitored at various temperatures and oxidizing environments, including dry oxygen and water vapor, up to atmospheric pressures. Based on this data, we have developed a semi-quantitative model of the initial oxidation stage where the dominant mechanism is oxygen diffusion on the Cu surface. We have compared our experimental data with Nucleation Rate theory, where our results suggest that nucleation rate theory qualitatively predicts the oxide nucleation behavior with respect to temperature and pressure. For real-world conditions, we have also focussed on passivation film formation due to oxidation in air at ambient temperatures. The classical theory of Cabrera-Mott describes passivation film formation on metals, where they predicted that this film grows as a uniform layer due to a field-enhanced ionic transport mechanism. Here we present experimental evidence that the passivation film nucleates and grows as oxide islands, not as a uniform layer. We propose an alternative phenomenological theory to describe passivation film formation, based on island growth followed by coalescence.

2:15 PM L2.3

A NOVEL METHOD FOR TRUE WORK FUNCTION DETERMINATION OF METAL SURFACES BY COMBINED KELVIN PROBE AND PHOTOELECTRIC EFFECT MEASUREMENTS. Bert Lagel, Iain D. Baikie, Konrad M. Dirscherl, Uwe Petermann, Robert Gordon Univ, Dept of Applied Physics, Aberdeen, UNITED KINGDOM.

We have developed a novel method for in-situ measurements of the true work function (ϕ) of metal surfaces by combined ultra-high vacuum compatible Kelvin Probe and photoelectric effect measurements. The work function is an extremely sensitive parameter of surface condition and can be used to study oxidation and thin film growth on metal surfaces [1]. For example, the increase in ϕ due to oxidation of polycrystalline rhenium at 800K is 1.9 eV. The Kelvin Probe measures local work function differences between a conducting sample and a reference tip in a non-contact, truly non-invasive way over a wide temperature range. However, it is an inherently relative technique and does not provide an absolute work function if the work function of the tip (ϕ_{tip}) is not known. We present a novel approach to measure ϕ_{tip} with the Kelvin Probe using the photoelectric effect, thus combining the advantages of both methods to provide the absolute work function of the sample surface. We demonstrate the application of the technique by in-situ work function measurements of evaporated thin films of rhenium and follow the oxidation kinetics of rhenium with oxygen exposure. The extended Kelvin Probe method therefore has potential applications as a characterisation tool for thin film epitaxy and work function engineering of surfaces. [1] I. Baikie, U. Petermann, B. Lagel, Surf. Sci. 433-435, 770 (1999)

3:00 PM *L2.4

ATOMIC MECHANISMS OF SURFACE ALLOY FORMATION. Andreas Schmid, Sandia National Laboratories, Livermore, CA.

Metals that do not form bulk alloys can often produce stable mixed phases at surfaces. Using prototypical examples to address surface alloy formation, this talk will highlight the importance of surface

adatoms and dislocations governing intermixing dynamics. Our experimental method is an adaptation of the classical approach of annealing diffusion couples: Time-dependent interdiffusion profiles across linear interfaces separating monolayer films of two different metals are measured by scanning tunneling microscopy. We find that the interdiffusion of Co and Cu in monolayer films on the Ru(0001) surface occurs through a combination of adatom surface diffusion and exchange of adatoms with atoms in the films. Further, the importance of dislocations in thin films was addressed by probing their influence on interdiffusion kinetics. As a test case, we studied intermixing between dislocated monolayer regions of Au adjacent to pseudo-morphic monolayer regions of Pd on Ru(0001). Dramatic interface motion and pronounced anisotropy of interdiffusion were found. We show how these unusual effects result from the dynamic behavior of dislocations present in the films and how they can be described by incorporating a source term into the usual diffusion equation.

3:30 PM *L2.5

STRUCTURAL AND MAGNETIC PROPERTIES OF SELF-ASSEMBLED LATERAL MULTILAYERS. E.D. Tober, Lawrence Berkeley National Laboratory; R.F. Marks; IBM Almaden Research Center; K. Roche, IBM Almaden Research Center; M. Toney, IBM Almaden Research Center; F.J. Palomares, ICM, Madrid, SPAIN; D.D. Chambliss, IBM Almaden Research Center; R.F.C. Farrow; IBM Almaden Research Center

The angular dependent magnetoresistance, magnetization, and growth of epitaxial $\text{Fe}_{\text{eta}}\text{Ag}_{1-\text{eta}}$ self-assembled lateral multilayers¹ (SALMs) have been examined in order to explore the interplay of structure and magnetism for these unique systems. SALMs consist of epitaxial thin film alloys of immiscible metals grown on $\text{Mo}(110)/\text{Al}_2\text{O}_3(11-20)$ template layers and display a unique form of compositional ordering not observed in the bulk. These systems are observed to form a compositionally ordered alloy of alternating, contiguous stripes of Fe (or Co) and Ag with the long axis of the stripe coinciding with the $\text{Mo}[001]$ direction in the plane of the substrate. The average stripe periodicities are on the order of 1.8 to 3.6 nm along the $\text{Mo}[110]$ (perpendicular to the stripes) direction depending on film stoichiometry and thickness as observed by STM, LEED, and TEM. The magnetization of these films as measured by MOKE and VSM is found to be highly anisotropic with the easy direction lying in-plane parallel to the $\text{Mo}[001]$ direction. The low temperature anisotropic magnetoresistance (AMR) and low field magnetoresistance (MR) are examined as a function of field angle for two nearly orthogonal current directions equivalent to the CPP and CIP configurations. The SALM structures are observed to display a significant AMR of nearly 10% for the entire structure. Furthermore, a pronounced MR is observed with a maximum DR/R of 0.88% ($\sim 29\%$ in the active layer) at 2.7 K.

¹"Self-assembled lateral multilayers from thin film alloys of immiscible metals", E.D. Tober, R. Farrow, R. Marks, K. Kalki, G. Witte, and D.D. Chambliss, Phys. Rev. Lett. 81 N9, 1897.

4:00 PM L2.6

THICKNESS DEPENDENT TETRAGONAL RELAXATION OF IRON IN EPITAXIAL Fe/Pd MULTILAYER FILMS. Ch. Muller, H. Muhlbauer, T. Steffl, B. Rellinghaus and G. Dumpsch, Experimentelle Tieftemperaturphysik, Gerhard-Mercator University, Duisburg, GERMANY.

The preparation of magnetic multilayers (ML) with iron is of interest, since it allows for the preparation of metastable fcc iron ($\gamma\text{-Fe}$), which is expected to undergo a volume-mediated change from antiferromagnetic order with low magnetic moment (LM) to ferromagnetic order with high magnetic moment (HM). Recently, we have shown that in polycrystalline $[\text{Fe}/\text{Pd}]_n$ MLs, iron grows up to 10 monolayers in the fcc phase exhibiting a moment of $2.7\mu_B$, whereas for thicker Fe layers, the bcc structure ($\alpha\text{-Fe}$) becomes more stable and the moment is reduced to the bulk value of $2.2\mu_B$ [1]. To shed more light on the details of this structural transition of the iron layer we have prepared epitaxially grown Fe/Pd MLs on sapphire.

Pre-seeding the sapphire substrate [a-plane, (1120)-orientation] with 0.5nm Fe at RT leads to a (001)-orientation of a subsequently grown Pd buffer layer ($t_{\text{buf}} = 30\text{nm}$, $T_{\text{growth}} \approx 700\text{K}$). $[\text{Fe}_t/\text{Pd}_{4n\text{m}}]_n$ ML stacks are then grown onto the Pd-buffered substrates with the iron layer thickness ranging from $t = 0.1\text{nm}$ to $t = 4\text{nm}$. We have monitored the growth in-situ via RHEED and STM. In addition, readily prepared MLs are characterized ex-situ by means of XRD and (HR)TEM on cross section samples. We find that epitaxy is preserved throughout as many as $n = 32$ periods within the ML stacks, though STM images clearly show a significant roughness in the films. RHEED patterns (3-dim. diffraction) evidence that with increasing thickness of the Fe layer, its lattice is successively tetragonally compressed along the growth direction, whereas the in-plane lattice constant remains unaltered. The Fe atomic volume is thereby decreasing from values larger than that of HM $\gamma\text{-Fe}$ to values smaller than that of bulk $\alpha\text{-Fe}$. The effect on the magnetic properties of the samples is discussed.

[1] H. Mühlbauer, Ch. Müller, and G. Dumpich, J. Magn. Magn. Mat. **192** (1999) 423.

4:15 PM L2.7

THE ROLE OF STRAIN IN THIN FILM ALLOY THERMODYNAMICS: COMPETITION BETWEEN ALLOYING AND DISLOCATION FORMATION. Gayle E. Thayer, UC Davis, Dept of Physics, Davis, CA; Andreas K. Schmid, N.C. Bartelt, V. Ozolins, M. Asta, J.J. Hoyt, Sandia National Labs, CA; S. Chiang, UC Davis, Dept of Physics, Davis, CA; R.Q. Hwang, Sandia National Labs, CA.

It has long been known that the structure of materials in thin film configurations can differ tremendously from their bulk phase. This is particularly true of alloy films. In particular, it has recently been shown that strain induced by the lattice mismatch between substrate and film can lead to the formation of novel alloys that do not exist in the bulk. A prototypical example is the system of one monolayer Ag/Co films grown on Ru(0001). In the bulk, Ag and Co are immiscible. However, on the Ru surface, alloy phases of distinct stoichiometries are formed. Phase segregation between a pure Ag phase containing dislocations and a pseudomorphically strained $\text{Co}_{0.6}\text{Ag}_{0.4}$ phase has been found. The driving force for segregation is the competition between two strain relief mechanisms. In the pure Ag phase, strain is relieved by dislocation formation. In the Co-rich alloy phase, strain is relieved by forming neighboring regions of both Ag and Co which experience opposite signed strain relative to the Ru substrate. This has been predicted by first principles calculations for pseudomorphic films. These predictions have been quantitatively compared to the experiment by measurements of the atomic strain at the interface between the Ag and Co regions in the alloy phase.

4:30 PM L2.8

ELABORATION OF SINGLE CRYSTALLINE $\text{Au/Ni}_{80}\text{Fe}_{20}/\text{Cu/Ni}_{80}\text{Fe}_{20}/\text{NiO}(111)$ SPIN VALVES. Antoine Barbier, Cristian Mocuta, Sébastien Lafaye, Pascale Bayle-Guillemaud, Département de Recherche Fondamentale sur la Matière Condensée, Grenoble, FRANCE.

NiO is a highly corrosion-resistant antiferromagnet. NiO(111)-based spin valves are interesting field sensors which could be used in hard drive read-heads, permanent magnetic memories as well as in harsh environments applications. Since spin valves are complex structures the understanding of the role of each layer (or interface) with respect to the general behavior is of high interest. We will show that high quality NiO(111) single crystal polar surfaces can be obtained. They are always stabilized by a $p(2 \times 2)$ reconstruction. These surfaces allowed the investigation of the growth of permalloy (Py, $\text{Ni}_{80}\text{Fe}_{20}$) on NiO(111), with respect to the growth temperature, by grazing incidence X-ray diffraction. This technique offers a main advantage: it is not limited by the charge build-up; the experiments were performed at the European Synchrotron Radiation Facility in Grenoble, France. The Py layer build on the NiO(111) single crystal behaves like a hard magnetic material because of the interfacial exchange coupling. Growth conditions in which the whole spin valve (in which the second Py layer is the sensing soft magnetic layer) is epitaxial were determined, giant magnetoresistances (GMR) of 3% at room temperature were observed easily on these structures without optimizing the thickness of the different layers. Energy filtered transmission electron microscopy (TEM) and high resolution TEM allowed understanding how deviations from the epitaxial growth regime prevent the onset of the GMR. These results open the possibility to study fully epitaxial spin-valves in order to understand better the exchange coupling occurring at ferromagnet/antiferromagnet interfaces.

4:45 PM L2.9

INTERFACIAL ENERGIES OF METALS ON OXIDES BY STM: Ag AND Cu ON $(1 \times 1)\text{-TiO}_2(110)$. S.M. Seutter, M.C. Bartelt, R.Q. Hwang, K.F. McCarty, Sandia National Laboratories, Livermore, CA; D.A. Chen, Dept of Chemistry and Biochemistry, Univ of South Carolina, Columbia, SC; D.R. Jennison, Sandia National Laboratories, Albuquerque, NM.

An important issue in heteroepitaxy and materials-joining technologies is the interfacial energy between overlayer and substrate. For example, the smaller the interfacial energy, the stronger the adhesion at the interface. For many metal-on-oxide systems, interfacial energies have not been determined. We demonstrate that scanning tunneling microscopy (STM) has been used to measure interfacial energies of Ag and Cu films on $\text{TiO}_2(110)$ surfaces. Submonolayer coverages (0.1 to 0.3 monolayers) of Ag or Cu were first evaporated onto $(1 \times 1)\text{-TiO}_2(110)$ at room temperature (RT) in ultra-high vacuum (UHV). The surface was then annealed to 850K for 1 minute to form equilibrium, faceted metal islands with diameters of 10 to 15 nm and heights of 1 to 2 nm, as observed by STM at RT in UHV. Larger islands could not be obtained with longer or higher temperature anneals. From STM height profiles of the islands, a Wulff

analysis was used to estimate interfacial energies, assuming Cu and Ag islands have top (111) facets with surface energies of $\sim 2 \text{ J/m}^2$ and $\sim 1.2 \text{ J/m}^2$, respectively [1], and the $\text{TiO}_2(110)$ substrate has a surface energy of $\sim 0.7 \text{ J/m}^2$ [2]. We find unexpectedly low values of $0.3 \pm 0.2 \text{ J/m}^2$ for Cu/ $\text{TiO}_2(110)$ and $0.5 \pm 0.2 \text{ J/m}^2$ for Ag/ $\text{TiO}_2(110)$, as compared to other metal-on-oxide systems. These values are close to predictions from first-principles density functional theory, within the generalized gradient approximation, using a large supercell to approximate an incommensurate interface [3]. We also discuss the nature of such strong adhesion of Cu and Ag on $(1 \times 1)\text{-TiO}_2(110)$. This work was supported by the USDOE-OBES, Division of Materials Sciences, under contract number DE-AC04-94AL85000. [1] L. Vitos et al., Surf. Sci. 411 (1998) 186. [2] S.P. Bates, G. Kresse, and M.J. Gillan, Surf. Sci. 385 (1997) 386. [3] P. Lu and F. Cosandey, Interface Science 2 (1994) 169.

SESSION L3: IN-SITU STUDIES OF COMPLEX OXIDE GROWTH ON OXIDE SUBSTRATES

Chairs: Rodney McKee and Mark Yeadon
Tuesday Morning, April 25, 2000
Salon 10/11 (Marriott)

8:30 AM *L3.1

THE IMPORTANCE OF *IN SITU* MONITORS IN THE PREPARATION OF LAYERED OXIDE HETEROSTRUCTURES BY REACTIVE MBE. D.G. Schlom, J.H. Haeni, C.D. Theis, Department of Materials Science and Engineering, Penn State University, University Park, PA; W. Tian, X.Q. Pan, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI; G.W. Brown, M.E. Hawley, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM.

Molecular beam epitaxy (MBE) has achieved unparalleled control in the integration of semiconductors at the nanometer level; its use for the integration of oxides with similar nanoscale customization appears promising. This talk will describe the use of reactive MBE to synthesize layered oxide heterostructures including new compounds and metastable superlattices. We will illustrate how combinations of *in situ* RHEED, atomic absorption spectroscopy (AA), a quartz crystal microbalance (QCM), and adsorption-controlled growth conditions have allowed the controlled synthesis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-SrTiO}_3$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-PbTiO}_3$ Aurivillius phases, $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper phases, and metastable $\text{PbTiO}_3 / \text{SrTiO}_3$ and $\text{BaTiO}_3 / \text{SrTiO}_3$ superlattices. The controlled synthesis of such layered oxide heterostructures offers great potential for tailoring the superconducting, ferroelectric, and dielectric properties of these materials. Structural and electrical characterization will be presented including *in situ* RHEED, 4-circle x-ray diffraction analysis, AFM, and high-resolution TEM images. Comparisons between the growth of compound semiconductors and oxides by MBE will be made. The importance of the underlying substrate and its preparation will be highlighted.

9:00 AM L3.2

OXIDATION KINETICS DURING OXIDE EPITAXY STUDIED BY AN OBLIQUE-INCIDENCE OPTICAL REFLECTIVITY DIFFERENCE TECHNIQUE. Xiangdong Zhu, University of California, Dept. of Physics, Davis, CA; Weidong Si, X.X. Xi, Qi Li, Penn State University, Dept. of Physics, University Park, PA; Qidu Jiang, M.G. Medici, University of Houston, Dept. of Physics, Houston, TX; Guo-zhen Yang, Huibin Lu, Fan Chen, Zheng-hao Chen, Institute of Physics, Chinese Academy of Sciences (CAS), Beijing, PR CHINA.

We studied oxidation kinetics in the epitaxy of SrTiO_3 , $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_{3-\delta}$ (LBMO), and $\text{SrTi}_{0.9}\text{Nb}_{0.1}\text{O}_3$ on $\text{SrTiO}_3(001)$ during pulsed laser deposition. By monitoring the linear optical response of an as-deposited monolayer oxide with an oblique-incidence reflectivity difference technique, we were able to determine the kinetics of oxidation of the monolayer with the ambient oxygen. We find the kinetics to vary from oxide to oxide over a wide range. As a result, epitaxial oxide films grown at a rate of a fraction of monolayer per second can easily have a high degree of oxygen deficiency relative to the state of the thermodynamic equilibrium under the growth conditions. We also found that at sufficiently high temperatures, the oxygen in the $\text{SrTiO}_3(001)$ substrate is mobile enough to move to the surface and oxidizes the more oxygen-deficient oxide overlayer, even in the absence of ambient oxygen. We present both the experiment and a simple theoretical model that describes the temperature and oxygen pressure dependence of the oxidation.

9:15 AM *L3.3

ATOMIC LAYER CONTROL OF EPITAXIAL $\text{SrRuO}_3\text{-SrTiO}_3\text{-SrRuO}_3$ HETEROSTRUCTURES ON TiO_2 -TERMINATED $(001)\text{-SrTiO}_3$ SUBSTRATES BY IN-SITU HIGH PRESSURE RHEED.

C.B. Eom, J.H. Choi, J.S. Noh, Duke University, Department of Mechanical Engineering and Materials Science, Durham, NC; A.J.H.M. Rijnders, F.J.G. Roesthuis, D.H.A. Blank, University of Twente, Department of Applied Physics, Enschede, THE NETHERLANDS; J.Z. Sun, IBM-T.J. Watson Reserch Center, Yorktown Heights, NY.

Atomic scale control of epitaxy in complex oxide heterostructures is very important for the fabrication of novel devices and the understanding of solid state phenomena. We have grown SrRuO₃-SrTiO₃-SrRuO₃ epitaxial heterostructures on perfect TiO₂-terminated (001) SrTiO₃ substrates using pulsed laser deposition including in-situ high pressure RHEED. SrRuO₃ is an ideal system to study the hetero-epitaxial growth mechanism of various perovskite thin films and to fabricate high quality multilayered devices. SrRuO₃ is a conductive ferromagnetic oxide with a lattice parameter of 3.93Å, i.e., a lattice mismatch with (001) SrTiO₃ substrates of 0.64%. AFM studies revealed that the surface morphology of each layers is extremely smooth with only steps of one-unit cell height, without any step bunching. Furthermore, sharp 0th-order Bragg reflections in the RHEED pattern and very low diffuse background intensity confirm the perfect crystalline surface. Our RHEED intensity data and AFM images suggest that the SrRuO₃ films on SrTiO₃ substrate grow in the step-flow mode with a transition from 2-dimensional layer-by-layer mode into step-flow mode after covering one monolayer of SrRuO₃. In contrast, the SrTiO₃ films on SrRuO₃ grow in the two-dimensional layer-by-layer mode. Such an atomic scale control of the interfaces and barrier layers in ferromagnetic oxide (FM-I-FM) trilayer junctions allows for quantitative studies of spin-polarized transport across the ferromagnetic oxide (FM-I-FM) trilayer junction interface, which will be discussed.

9:45 AM L3.4

TIME RESOLVED STUDIES OF SrTiO₃ HOMOEPITAXY BY SYNCHROTRON X-RAY SURFACE DIFFRACTION. G. Eres, J.D. Budai, B.C. Larson, D.H. Lowndes, C.M. Rouleau, J.Z. Tischler and M. Yoon, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; P. Zschack, UNICAT, University of Illinois at Urbana-Champaign, Urbana, IL.

The ability to monitor the evolution of atomic scale surface structure in real-time facilitates fundamental studies of the mechanisms that govern thin film growth processes. The high brilliance of third-generation synchrotron light sources provides dramatically increased count rates that enable time dependent measurements of the interference between the substrate and the over layer at the weakly scattering crystal truncation rods (CTR). In this paper we describe application of synchrotron x-ray surface diffraction in time resolved studies of SrTiO₃ homoepitaxy by pulsed laser deposition. The intermittent nature of the laser ablation process allows measurements of the surface structure during and after the arrival of the ablation plume. The evolution of the crystalline structure was deduced from measurements of in-plane reflections ($h, k \neq 0$) and specular ($h = k = 0$) CTR reflections. The in-plane measurements provide information on the incorporation of atoms parallel to the surface, and the specular reflections provide information about their relative location perpendicular to the surface. The experimental results will be compared with modeling studies addressing the observed time dependence in terms of the surface disorder resulting from the arriving plume, and the subsequent recovery governed by the balance between diffusion and ordering kinetics.

SESSION L4: EPITAXIAL GROWTH OF OXIDES ON OXIDE SUBSTRATES

Chairs: Jerry Hallmark and Mark Yeadon
Tuesday Morning, April 25, 2000
Salon 10/11 (Marriott)

10:30 AM L4.1

GROWTH DEPENDENT H-DEPENDENT MAGNETIC DOMAIN STRUCTURES IN La_{0.67}Sr_{0.33}MnO₃ THIN FILMS. M.E. Hawley, G.W. Brown, P.C. Yashar and C. Kwon, Los Alamos National Lab, Los Alamos, NM.

Maze- and bubble-like magnetic domain structures have been observed under ambient conditions in La_{0.67}Sr_{0.33}MnO₃ (LSMO) films by magnetic force microscopy (MFM) for films grown on a compressive (LaAlO₃) lattice-mismatched substrate. In this study, we have examined films grown at 550°C to 800°C by pulsed-laser deposition by scanning tunneling and magnetic force microscopy to obtain both microstructure and domain structures. Grain size was found to correlate with coercivity measured by VSM. Substrate-induced stress and growth related microstructure in this soft magnetic material was found to be responsible for the appearance

and nature of magnetic structures. The stress was reflected in distortions to the unit cell measured by x-ray diffraction. In addition, the magnetic structures were studied as a function of in-plane magnetic field strength. Also, films nominally grown under the same conditions, possessed subtle differences in domain structure and wall spacing, the latter due in part to differences in film thickness. As the field was increased, the maze-like structures transformed into stripe domains with reduced out-of-plane magnetization and decreased wall spacing. These observations were consistent with parallel rather than antiparallel alignment of in-plane spin polarization. After removal of the field, the stripe domains remained but the wall spacing and z polarization component returned to the original value. For one 800°C the field-dependent magnetic structures were correlated to VSM data. The changes in the magnetic structure correlated directly with the nonideal hysteretic magnetization behavior. Wall motion was responsible for the rounding in the VSM curves. A comparison was made between the form film and one capped by a thin insulating cap layer where the domains were pinned in the remanent state.

10:45 AM *L4.2

EPITAXIAL TIN DIOXIDE THIN FILMS ON THE SAPPHIRE SUBSTRATE BY ULTRAFAST LASER ABLATION DEPOSITION. X.Q. Pan and L. Fu, Dept. of Materials Sci. & Eng., University of Michigan, Ann Arbor, MI; P. Pronko, Center for Ultrafast Optical Science, University of Michigan, Ann Arbor, MI.

Owing to its high sensitivity to small concentrations of chemical gases as well as high chemical and mechanical stability, SnO₂ with the rutile structure is widely used as a base material in chemical sensors. In particular, SnO₂ thin films have recently drawn much interest because of their potential application in microsensor devices. In this paper we report our experimental results on the synthesis and characterization of SnO₂ epitaxial thin films on sapphire substrates. The SnO₂ thin films were deposited on the sapphire substrates with different surface orientations by a pulsed laser deposition using a femtosecond laser. The energy distribution of ions and neutral atoms in the ablation plume is analyzed using an ion energy spectrometer. The ion spectra provide information on the Sn/O ratio of the ablation plume, prior to its being mixed with the background discharge oxygen gas. The on-line plasma and plume diagnostics also gives information on how isothermally regulated the plume remains as it moves toward the substrate. Thin film microstructures were investigated by both x-ray diffraction and transmission electron microscopy techniques. It was found that the SnO₂ thin films grown on the (10-12) surface of sapphire substrate are epitaxial, single crystal, while those films on the (0001) surface of sapphire consist of textured structures with both (101) and (200) oriented grains. The epitaxial growth mechanisms of SnO₂ thin film will be discussed based on the analysis of the ablation plume - substrate interaction and the film/substrate lattice mismatch.

11:00 AM L4.3

Abstract Withdrawn.

11:15 AM L4.4

THE EFFECT OF MgO BUFFER ON THE EPITAXIAL GROWTH OF ZnO ON Al₂O₃(0001). Yefan Chen, Hang-ju Ko, Soon-ku Hong, Takashi Hanada and Takafumi Yao, Institute for Materials Research, Tohoku University, Sendai, JAPAN; Yusaburo Segawa, PhotonDynamics Research Center, Institute for Physical and Chemical Research, Sendai, JAPAN.

Among wide bandgap semiconductors, ZnO is characterized by its direct bandgap in UV region, the strongest bond strength among II-VI semiconductors and very large exciton binding energy of 60 meV. Recent studies showed that the extremely stable excitons, which survive well at room temperature, enable ZnO a promising material for applications to low-threshold excitonic lasers. To date, because of the absence of suitable substrate materials, main efforts on ZnO epitaxial growth have been concentrated on Al₂O₃(0001) substrate. However, because of the large lattice and thermal mismatch, ZnO films grown on Al₂O₃(0001) showed poor surface morphology and crystal quality. In the present paper, we demonstrate how to improve of surface morphology and crystal quality of ZnO epilayer by using a thin MgO buffer. Since MgO itself is an II-VI oxide compound, the growth is carried out in the same chamber for growing ZnO without inter-contamination problem. Also there is no additional problem in device design caused by a MgO layer, which is completely transparent at the wavelength where ZnO based devices works. The ZnO films are grown on widely used low cost sapphire substrate by plasma assisted molecular beam epitaxy. The thin MgO buffer is very effective on the improvement of surface morphology during initial growth stage, which eventually leads to an atomically flat surface. As a result, (3x3) surface reconstruction of ZnO is observed and reflection high-energy electron diffraction intensity oscillation is recorded on ZnO, which indicates the achievement of layer-by-layer growth. Structural analysis indicates that the twin defect with a 30° in-plane crystal orientation mis-aligning is completely eliminated, meanwhile the total dislocation

density is reduced much. Free exciton emissions at 3.3774 eV (XA) and 3.383 eV (XB) are observed in photoluminescence at 4.2 K further indicating the high quality of the resulting ZnO epilayers.

11:30 AM L4.5

DEFECTS AND STRUCTURE OF INTERFACE IN $Mg_xZn_{1-x}O/\alpha-Al_2O_3$ HETEROSTRUCTURES. A. Kvit, A.K. Sharma and J. Narayan, Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC.

Recently, ZnO has attracted attention not only as a suitable closely lattice-matched substrate for GaN but also as a potentially useful active optoelectronic material itself. This raises new questions not only about the basic properties of ZnO but also about those of related materials that can be alloyed with ZnO in heteroepitaxial device structures. One would need a material with a higher band gap to use as barrier in order to make ZnO quantum wells. Recently it was shown that it is possible to grow $Mg_xZn_{1-x}O$ alloy films with wurtzite structure over a certain range of concentrations up to 50%. In this work, we report the transmission microscopy study of typical extended defects and microstructural features in the epitaxial hexagonal $Mg_{0.36}Zn_{0.64}O$ and $Mg_{0.2}Zn_{0.8}O$ alloy films grown on $\alpha-Al_2O_3$ substrate. These layers were synthesized by pulsed laser deposition using KrF excimer laser in high vacuum chamber. The temperature of substrate varies in the range 700 -750 °C for optimization of growth parameters. The PLD films were found to be single crystalline structure with high concentration of dislocation up to $10^{10} cm^{-2}$ at a film thickness 1 μm . The typical structure of defects and interfaces in these films is analyzed and compared with ZnO epitaxial films grown at the same conditions. It was found a 30° rotation of ZnMgO basal planes with respect to sapphire substrate that is similar to ZnO/Sapphire growth. In contrast to ZnO/Sapphire we do not observe stacking faults in high concentration in ZnMgO epitaxial films. Finally, the evolution of extended defect density with thickness and time of annealing was investigated.

11:45 AM L4.6

EPITAXIAL GROWTH OF Co_3O_4 THIN FILMS BY LOW TEMPERATURE, LOW PRESSURE MOCVD. K. Shalini, Anil U. Mane, R. Lakshmi, S.A. Shivashankar, Indian Institute of Science, Materials Research Centre, Bangalore, INDIA; M. Rajeswari, Univ. of Maryland, Dept. of Physics, College Park, MD.

Strongly oriented or epitaxial growth of thin films of metal oxides generally requires relatively high growth temperatures or infusion of energy to the growth surface through means such as ion bombardment during film growth. We have grown epitaxial thin films of the cubic oxide Co_3O_4 on different substrates at temperatures as low as 450°C by low pressure metalorganic chemical vapor deposition (MOCVD) using a cobalt β -diketonate complex as the CVD precursor and argon as the carrier gas for the sublimed vapors. When oxygen is used as the reactive gas, polycrystalline films of Co_3O_4 are formed at temperatures ranging from 400-500°C on glass and Si{100} substrates, at a total pressure of about 600 Pa. Under similar conditions of growth at 450°C, epitaxial films of Co_3O_4 with {100} orientation are formed on single crystal SrTiO₃{100}. A film grown simultaneously on LaAlO₃{100} substrate is also epitaxial, having the {110} orientation. The crystalline quality of the films (out-of-plane texturing and in-plane alignment) was determined by 4-circle x-ray diffraction. The films on SrTiO₃{100}, as grown, show rocking FWHM ~ 0.33 degree, which is comparable to the best values in epitaxial perovskite oxide films grown at significantly higher temperatures. The rocking angle widths of the films on LaAlO₃{100} are somewhat larger - 1.65 degree for as-grown films. In an attempt to improve the epitaxy, the films were annealed at 725°C in oxygen. The rocking FWHM of the annealed films improves to 0.29 degree on SrTiO₃{100}, and to 1.3 degree on LaAlO₃{100}. On both these substrates, phi scan analysis indicates epitaxial in-plane alignment of the films with the substrate for both as-grown and annealed films. Details of the epitaxial alignment on the two substrates will be presented. A mechanism for the observed low temperature epitaxy will be proposed.

SESSION L5: IN-SITU STUDIES OF OXIDE GROWTH ON SILICON

Chairs: Marilyn E. Hawley and Orlando Auciello
Tuesday Afternoon, April 25, 2000
Salon 10/11 (Marriott)

1:30 PM *L5.1

STUDIES OF FERROELECTRIC THIN FILM GROWTH AND SURFACE AND INTERFACE PROCESSES VIA IN SITU ELLIPSOMETRY, TIME-OF-FLIGHT ION SCATTERING, AND DIRECT RECOIL SPECTROSCOPY IN WIDE RANGE PRESSURE ENVIRONMENTS. A.R. Krauss, A.M. Dhote, Argonne National Laboratory, Materials Science and Chemistry Divisions,

Argonne, IL; O. Auciello, J. Im, Argonne National Laboratory, Materials Science Division, Argonne, IL; E.A. Irene, Y. Gao, A.H. Muller, University of North Carolina, Dept of Chemistry, Chapel Hill, NC; S. Aggarwal and R. Ramesh, University of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD.

The science and technology of ferroelectric and high dielectric constant thin films has experienced an explosive development during the last ten years. Low-density non-volatile ferroelectric random access memories (NVFRAMs) are now incorporated in commercial products such as smart cards and cellular phones. In addition, high dielectric constant thin films will be introduced in the near future into DRAMs. However, substantial work remains to be done to develop materials integration strategies for high-density NVFRAMs and high permittivity DRAMs. We have demonstrated that the implementation of a variety of complimentary in situ or in situ, real-time characterization techniques is critical to understand film growth and post-deposition processes. We have developed a time of flight ion scattering and recoil spectroscopy (TOF-ISARS) technique to perform in situ, real-time studies of film growth processes in a wide range of background pressures from high vacuum to tens of millitorrs. TOF-ISARS involves three distinct but closely related experimental methods, namely: ion scattering spectroscopy (ISS), direct recoil spectroscopy (DRS) and mass spectroscopy of recoiled ions (MSRI), which are capable of providing monolayer-specific information on film growth and surface segregation processes in the ambient conditions required for growing ferroelectric and other oxide thin films. TOF-ISARS can monitor the surface composition and structure of thin films, but not buried interfaces. Therefore, we have combined TOF-ISARS with Spectroscopic Ellipsometry, which permits investigation of buried interfaces as they are being formed. Recent work performed to understand growth and post-deposition processes and microstructure-property relationships of layered perovskite SrBi₂Ta₂O₉ (SBT) and Ba_xSr_{1-x}TiO₃ (BST) thin films will be discussed.

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2:00 PM *L5.2

IN SITU REAL-TIME STUDIES OF COMPLEX OXIDE FILMS FOR ELECTRONIC APPLICATIONS. Eugene A. Irene, Dept. of Chemistry, University of North Carolina, Chapel Hill, NC.

Modern electronic materials applications such as MOSFET's require the use complex oxide films for gate dielectrics and storage capacitors in conventional MOSFET's, and as polarizable media in ferroelectric based MOSFET's. Because of the level of perfection required for these applications, the film deposition processes must be monitored and controlled in terms of the film composition, structure and morphology. In addition for very thin films the process dynamics is also crucial, in order to reliably obtain the correct film thicknesses. Barrier films will be required which obviate reaction of the complex oxide with a variety of substrates and contact material. On the scientific side the details of interface reactions between complex oxide films and substrates are difficult to study because the growing film covers the interface. In order to address all these issues we have developed a world-wide unique deposition and characterization system as a collaboration between UNC, Argonne National Laboratory, ANL and Ionwerks Inc. This system comprises a vacuum chamber multi target sputter ion deposition subsystem with spectroscopic ellipsometry (SE) and time of flight ion scattering and recoil spectroscopy (TOF-ISARS). Characterization can be performed during film growth and annealing processes. In this review this unique system will be briefly discussed, and the most recent results of in situ real-time complex oxide film growth dynamics, interface reactions, film structure, morphology and barrier film stability will be presented. Examples will be presented from silicon, ferroelectric and device contact research areas during the ongoing collaborative studies.

2:30 PM L5.3

IN-SITU STUDY OF BARRIER LAYERS USING SPECTROSCOPIC ELLIPSOMETRY AND MASS SPECTROSCOPY OF RECOILED IONS. Y. Gao, A.H. Mueller, E.A. Irene, Department of Chemistry, University of North Carolina, Chapel Hill, NC; O. Auciello, A.R. Krauss, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL; J.A. Schultz, Ionwerks, Houston, TX.

With the miniaturization of modern devices, more complex multilevel

structures are required for the fabrication of electrical contacts, and different new materials need to be integrated into the technology, in order to optimize the device performance. Both the proximity and diversity increase the possibility of interdiffusion and/or chemical reactions between multilayer thin film materials. Barrier films help to reduce these unwanted interreactions. Hence, a rapidly growing number of studies have been devoted to evaluate the stability and barrier properties of a wide variety of materials. However, most of these analyses have been performed with ex-situ and/or using destructive techniques, such as Rutherford back-scattering spectroscopy (RBS), X-ray diffraction (XRD), Auger electron spectroscopy (AES) depth profile, transmission electron microscopy (TEM) and electrical measurements. The objective of this study is to demonstrate an in-situ real time methodology to monitor the evolution of barrier effectiveness. In this paper, it will be shown that spectroscopic ellipsometry (SE) and differentially pumped mass spectroscopy of recoiled ions (MRSI) enables the detection of barrier layer performance under processing conditions. As examples, we will present new results of in-situ studies of the interdiffusion and interreaction between Cu/Si with/without a Ta-Si-N barrier layer; as well as the thermal stability study of the barrier layer for BST high K dielectric films with Ir electrodes in dynamic random access memory (DRAM) device structures.

SESSION L6: EPITAXIAL GROWTH OF OXIDES ON SILICON

Chairs: Darrell G. Schlom and Orlando Auciello
Tuesday Afternoon, April 25, 2000
Salon 10/11 (Marriott)

3:15 PM *L6.1

STRUCTURE OF THE SILICON-OXIDE INTERFACE. Yuhai Tu and J. Tersoff, IBM-T.J. Watson Research Center, Yorktown Heights, NY.

Interfaces between crystalline and amorphous materials play a crucial role in devices and device fabrication. The most important example is undoubtedly the interface between crystalline Si and its amorphous native oxide SiO₂. This remarkable interface is the basis for most current computer technology, yet its structure remains poorly understood. We have developed a new computational approach to this problem, which explicitly averages over the ensemble of configurations of the amorphous oxide. The approach makes possible the first calculation of equilibrium interface structures and energies for an amorphous-oxide interface. This talk describes our method, and presents a model for the Si-SiO₂ interface that has low energy and reconciles a variety of puzzling experimental results.

3:45 PM *L6.2

HETEROEPITAXY AT AN OXIDE/SEMICONDUCTOR INTERFACE – A CORRELATION BETWEEN PHYSICAL AND ELECTRICAL STRUCTURE. Rodney McKee, Oak Ridge National Laboratory, Oak Ridge, TN.

The fundamental interests in oxide/semiconductor heteroepitaxy primarily reside in development of an understanding of length scale issues. Chemical bonding and crystal symmetry are overarching constraints on whether a commensurate interface develops between the dissimilar materials and two cases will be discussed in this talk: BaSrO and SrTiO₃ on silicon and BaO and BaTiO₃ on germanium. We will present an experimental study and results in which commensurate heteroepitaxy can be obtained in these systems, and use simple oxide/semiconductor capacitors to demonstrate the coupling between the physical and electrical structure at the interface. The utility of such experiments goes directly at the question of whether an alternative to the SiO₂ dielectric on silicon can be obtained using high performance crystalline oxides. Sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

4:15 PM L6.3

METAL-ORGANIC MOLECULAR BEAM EPITAXY OF MAGNESIUM OXIDE ON SILICON. F Niu, B.H. Hoernem and B.W. Wessels, Dept. of Materials Science and Engineering and Materials Research Center, Northwestern University, Evanston, IL.

Epitaxial MgO films have been grown on single crystal Si (001) substrates by metal-organic molecular beam epitaxy using a solid precursor, magnesium beta-diketonate and activated oxygen. The process involved the growth of a thin epitaxial interlayer followed by deposition of MgO at 800 C. The overlayer was epitaxial with a MgO(001)//Si(001), MgO[110]//Si[110] orientation. The structure of the interlayer and oxide layer was characterized by RHEED and high-resolution transmission electron microscopy. The composition

was determined by Auger electron spectroscopy and Fourier transform infra-red spectroscopy. The formation of the interlayer and MgO was studied with RHEED.

4:30 PM PANEL DISCUSSION

SESSION L7: EPITAXY OF OXIDES ON SILICON

Chairs: Jeffrey W. Bullard and Bruce W. Wessels
Wednesday Morning, April 26, 2000
Salon 10/11 (Marriott)

8:30 AM *L7.1

EPITAXIAL OXIDE FILMS ON SILICON: GROWTH AND MODELING. J.A. Hallmark, J. Wang, Z. Yu, R. Droopad, J. Ramdani, J. Curless, C.D. Overgaard, K. Eisenbeiser, J.M. Finder, D.S. Marshall, W.J. Ooms, Physical Sciences Research Labs - Motorola Labs, Tempe, AZ.

Epitaxial oxide high-k transistors could provide the platform for a new class of silicon transistors. SiO₂ gate oxide scaling is reaching a physical tunneling limit, and higher dielectric constant materials will be the gate insulator for future MOSFET devices. SrTiO₃ (STO) appears to be very promising due to its high dielectric constant and good insulating properties. Epitaxial oxide devices have not been practical to produce for a number of reasons, mainly relating to chemical and electrical problems at the interface between the oxide material and silicon. Recently, we have grown epitaxial STO directly on a Si (001) substrate using molecular beam epitaxy. The films show good interface and electrical properties. In this presentation, the basic material growth and resulting properties will be presented, along with modeling and characterization of our proposed interface structure.

9:00 AM L7.2

OPTICAL PROPERTIES OF BULK AND THIN-FILM SrTiO₃ ON Si and Pt. Stefan Zollner, A.A. Demkov, Ran Liu, P.L. Fejes, R.B. Gregory, P. Alluri, Motorola SPS, Mesa, AZ; Jay Curless, Z. Yu, J. Ramdani and R. Droopad, Motorola PSRL, Tempe, AZ; T.E. Tiwald, J.N. Hilfiker, J.A. Woollam, J.A. Woollam Co., Lincoln, NE.

Oxides with perovskite crystal structure are important candidates for ultrathin gate oxides because of their large DC dielectric constant. When SrTiO₃ is deposited directly on Si, an amorphous non-stoichiometric interface (10-30Å thick) is usually formed during the later stages of growth. This is undesirable, since it reduces the capacitance. Optical tools such as spectroscopic ellipsometry (SE) can easily be adapted for in-line or *in situ* diagnostics of SrTiO₃ on Si, therefore understanding the optical properties of such thin films is important. When we are interested in the properties of thin films, it is a good idea to start with studying the bulk. Following Jellison, we measured the dielectric function of bulk SrTiO₃ from 0.74 to 6.6 eV. We also performed measurements in the infrared and in the vacuum UV. In comparison with ab initio band structure calculations, we identify the critical points in the spectra at 3.78, 4.29, 4.76, and 6.15 eV due to interband transitions from the O (2p) valence band to the Ti (3d) conduction band. Unlike SrTiO₃ films grown on MgO, which have the same refractive index as bulk SrTiO₃, our thin SrTiO₃ films on Si have a lower refractive index. Since the films are smooth in AFM, this cannot be attributed to surface roughness. Spectroscopic ellipsometry cannot determine thickness and refractive index *n* independently for very thin layers, but rather measures an effective *n* averaging over the amorphous interface and the SrTiO₃ film. For film thicknesses between 160 and 200Å, *n* at 633 nm ranges from 2.1 to 2.2 (compared to 2.4 in the bulk). Thinner films (110-130Å) have an even lower *n* around 1.9. We propose that the amorphous interface has a lower *n* than bulk SrTiO₃ and therefore reduces the effective *n* with decreasing film thickness. For process control, one can try to minimize the interface thickness by maximizing *n*.

9:15 AM L7.3

TWO STEP PROCESS FOR THE GROWTH OF A THIN LAYER OF SILICON DIOXIDE FOR TUNNELLING EFFECT APPLICATIONS. Jorge Pedro, Hugo Aguas, Elvira Fortunato, Isabel Ferreira, Rodrigo Martins, New Univ. of Lisbon, Fac. of Science and Technology, Materials Science Dept., CENIMAT and CEMOP/UtNINOVA, Monte da Caparica, PORTUGAL.

In the SIS (Semiconductor-Insulator-Semiconductor) solar cells the insulator plays the main role in the device performances. It should be very thinner (below 4 nm thickness) and also compact, to form the desired tunnelling effect between the two semiconductor layers, the silicon and the semiconductor oxide. The silicon oxidation method proposed consists in a two step process. First the silicon wafer is oxidised in a furnace at a temperature of 560°C, using a mixture of oxygen and nitrogen gases. This permits a very slow oxidation that can be easily controlled by the time of oxidation. In spite of this,

ellipsometric measurements of this oxide revealed a poor compact oxide. To improve the compactness of the oxide, we use a second step process that consists in oxygen plasma treatment of the oxide, which under appropriate conditions can lead to the improvement of the compactness of the silicon dioxide film, as revealed by ellipsometric studies. These results, together with SIMS and RBS data, were correlated with the data obtained from the C-V measurements performed aiming to establish the best oxide properties and thickness that lead to the production of cheap and efficient solar cells.

9:30 AM L7.4

DEPOSITION OF CeO₂ THIN FILMS WITH (200) PREFERRED ORIENTATION ON Si(100) SUBSTRATE BY RF-MAGNETRON SPUTTERING. Leejun Kim, Jinmo Kim and Donggeun Jung, Dept of Physics, Sungkyunkwan Univ, Suwon, SOUTH KOREA.

In recent years, CeO₂ has been studied extensively due to its various applications. Because CeO₂ has a cubic crystal structure and the lattice constant of CeO₂ is close to that of Si, many research groups have attempted to grow epitaxial thin films of CeO₂ on Si substrates in order to produce the silicon-on-insulator (SOI) structures by deposition methods. In addition, CeO₂ was used as the intermediate layer between the ferroelectric thin film and the Si substrate in a metal-ferroelectric-semiconductor field effect transistor (MFSFET) to prevent the interdiffusion of the ferroelectric material and the Si substrate. For above applications, it is very important to investigate the crystal orientations of CeO₂ thin films deposited on Si substrates. There are many reports on the growth of CeO₂(111) layers on Si(111) substrates by e-beam evaporation and the laser ablation. These methods are very difficult to be used in large scale production lines, whereas radio-frequency (rf)-magnetron sputtering is widely used in large scale semiconductor processes. There have been very few reports on the growth of CeO₂ films with (200) preferred orientation by sputtering on Si(100) substrates, which are used much more than Si(111) substrates. In this work, we report on the effect of deposition parameters of rf-magnetron sputtering on the crystallinity of CeO₂ thin films on Si(100) substrates. Deposition temperature, rf-power and seed layer deposition time were important parameters effecting the crystallinity of CeO₂ thin films. The CeO₂(200) peak was notable for a deposition temperature above 600°C. With decreased rf-power and thus lower deposition rate, the intensity of the CeO₂(200) peak increased. When the seed layer deposition time was less than 20 sec, the CeO₂(200) peak dominated. By optimizing these parameters, CeO₂ thin films with a strongly preferred orientation in the (200) direction could be deposited on Si(100) substrates by rf-magnetron sputtering.

SESSION L8: EPITAXY OF OXIDES AND METALS

Chairs: Jeffrey W. Bullard and Bruce W. Wessels

Wednesday Morning, April 26, 2000

Salon 10/11 (Marriott)

10:15 AM L8.1

IN SITU, REAL TIME STUDIES OF OXYGEN INCORPORATION IN COMPLEX OXIDE THIN FILMS USING SPECTROSCOPIC ELLIPSONOMETRY AND ION SCATTERING AND RECOIL SPECTROMETRY. A.H. Mueller, Y. Gao, E.A. Irene, University of North Carolina at Chapel Hill, Dept of Chemistry, NC; O. Auciello, A.R. Krauss, Argonne National Laboratory, Material Science and Chemistry Division, Argonne, IL; J.A. Schultz, Ionwerks, Houston, TX.

The decrease in feature size of electronic devices and the commensurate electronic properties scaling has resulted in a search for new materials to achieve the electronic properties required for such miniature technologies. Complex oxide materials have exhibited the necessary properties for uses in such technologies as high K DRAM capacitors, Josephson junctions, SQUIDS, and ferroelectric devices. The properties of these films have shown a critical dependence on their oxygen content, such as loss of a superconducting transition by YBa₂Cu₃O_{7-x} (YBCO) depending upon the exact oxygen content, and the lowering of the dielectric constant of the high K material BaSrTiO₃ (BST) under oxygen deprived conditions. The objective of this study is to show the real-time mechanics of oxygen incorporation as well as the structural effects using real time, In-Situ Spectroscopic Ellipsometry (SE) and Ion Scattering and Recoil Spectrometry (ISARS). It has been shown that oxygen incorporation into complex oxide thin films can be followed in real time using SE, and that chemical and structural information such as oxygen adsorption and bonding sites may be obtained by the ISARS techniques. These complementary techniques are applied in real-time, and as such yield a wealth of information not only about the incorporation of oxygen, but also about the mechanism and structural effects relative to film function. The most recent resultson YBCO and BST will be presented.

10:30 AM L8.2

Mg GROWN ON MgO(001), (011), AND (111) STUDIED BY RHEED AND STM. Gung Chern, Nan-Ji Chen, Jia-Jiun Ka, National Chung-Cheng Univ, Dept of Physics, Chia-Yi, TAIWAN ROC.

Relative to alkali metals, the growth of alkaline earth metals including Mg has not been reported very much. In this study, Mg film grown on MgO(001), (011) and (111) with high crystalline quality is observed. In situ reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) are used to characterize the surface during the growth. A pseudomorphic structure of the Mg film is identified by RHEED until the film thickness reaches ~ 2 nm for all films. This metastable fcc phase is followed by the MgO template even though the close packed misfit is ~ 8%. After the film is thicker than 2 nm, it relaxes to hcp but with strong orientational dependence. We observed that it is rather straightforward for a fcc (111) switching to a hcp (0001) plane because both planes are close packed. On the other hand, fcc (001) and (011) have no corresponded planes in hcp structure. The RHEED shows a long intermediate stage ~20 nm before stable patterns with fractional order peaks are observed. We believe that it is related to a 6x1-unit cell, which results from a changing of ABCABC (two units of a fcc structure) to ABABAB (three units of a hcp structure) layer sequences. Although MgO substrate is highly insulating, a few tens nm thick Mg is able to have tunneling current to get STM images. The morphologies of the thicker film show interesting spiral-like, faceting, and terrace modes on the original (111), (110) and (001) planes, respectively. The oriented dependence of the morphology will be discussed.

10:45 AM L8.3

MICROSTRUCTURE OF Bi-Sr-Ca-Cu-O SUPERCONDUCTING FILMS DEPOSITED ON SILICON SUBSTRATES WITH YSZ BUFFER LAYERS. Qian Wensheng, Zhou Xing, School of Electrical & Electronic Engineering, Nanyang Technological University, SINGAPORE; Wei Tongli, Microelectronics Center, Southeast University, Nanjing, PR CHINA.

Bi-Sr-Ca-Cu-O (BSCCO) high T_c superconducting films is deposited on Si(100) substrates with YSZ buffer layers by single target rf magnetron sputtering. In growing process, off-axis technique is used to reduce the resputtering effect. The technique parameters including deposition temperatures, sputtering atmosphere and annealing conditions are obtained. The critical temperature of BSCCO film on YSZ/Si is 82K. Scan Electronic Microscope and Atomic Force Microscope are used to observe the surface morphologies of BSCCO/YSZ/Si. The spiral growth patterns of superconducting grains and the relation between superconducting phases and substrate temperatures are verified. The fractal growth is first found in BSCCO/YSZ/Si morphologies. The fractal dimension is 1.795. The geometry and crystal properties of fractal structure are studied. As the result, the fractal formation model in BSCCO/YSZ/Si in which diffusion and nucleation exist at the same time is presented and verified. It is also pointed out that the fractal formation appears in the annealing process and has close relation with crystallization of BSCCO films. The analyses of fractal formation mechanism break through the unitary diffusion way in DLA and KCA fractal models. This theory is helpful for the improvement of high T_c superconducting films.

11:00 AM L8.4

MICROSTRUCTURE AND PROPERTIES OF PbZr_{0.6}Ti_{0.4}O₃ AND PbZrO₃ THIN FILMS DEPOSITED ON TEMPLATE LAYERS. R.E. Koritala and M.T. Lanagan**, Energy Technology Division, Argonne National Laboratory, Argonne, IL; G.R. Bai, Y. Huang and S.K. Streiffer, Materials Science Division, Argonne National Laboratory, Argonne, IL. **Current address: Materials Research Laboratory, Pennsylvania State University, University Park, PA.

Polycrystalline PbZr_{0.6}Ti_{0.4}O₃ and PbZrO₃ thin films were deposited at low temperatures (450-525°C) on (111)Pt/Ti/SiO₂/Si substrates by metal-organic chemical vapor deposition. The film texture could be improved and lower deposition temperatures could be used by depositing the films on PbTiO₃ or TiO₂ template layers. Films were characterized by scanning and transmission electron microscopy and by X-ray diffraction; electrical properties were also examined. The microstructure and electrical properties of films deposited on both the original substrate and on the template layers were compared. Based on the results, possible nucleation and growth mechanisms have been proposed. Work supported by the U.S. Department of Energy, Office of Advanced Automotive Technologies, under Contract W-31-109-Eng-38.

11:15 AM L8.5

SOLUTION SYNTHESIS OF EPITAXIAL RARE-EARTH OXIDE THIN FILMS ON ROLL-TEXTURED NICKEL. Jonathan S. Morrell, Ziling B. Xue, University of Tennessee, Department of Chemistry, Knoxville, TN; David B. Beach, Catherine E. Vallet, Mariappan

Paranthaman, Thomas G. Chirayil, Oak Ridge National Laboratory, Chemical and Analytical Sciences Division, Oak Ridge, TN.

Using solution chemistry, epitaxial films of rare earth oxides of the general formula RE₂O₃ (where RE = Sm to Lu) were prepared on cubic-textured nickel tapes. Solutions of metal methoxyethoxides or metal acetate/methoxyethoxides in 2-methoxyethanol were used to coat roll-textured nickel tapes using either spin coating or dip coating. Coated tapes were subsequently heated in a reducing atmosphere at temperatures between 950 and 1150°C for varying lengths of time. Film quality was determined using X-ray diffraction and electron and surface probe microscopy. Films were found to be oriented both in and out of the plane of the substrate, free of pin-holes and gross defects, and of sufficient quality for use as substrates for high T_c superconductors.

This work was supported by the Division of Materials Sciences, Office of Science, U.S. Department of Energy and was performed at the Oak Ridge National Laboratory under contract DE-AC05-96OR22464 with the Lockheed Energy Research Corporation.

SESSION L9: IN-ROOM POSTER SESSION

Wednesday Morning, April 26, 2000

11:15 AM

Salon 10 (Marriott)

L9.1

STRUCTURE CHARACTERIZATION OF EPITAXIALLY STRAINED YBa₂Cu₃O₇/PrBa₂Cu₃O₇ SUPERLATTICES.

Maria Varela, Univ Carlos III de Madrid, Dept de Física, Leganès, SPAIN; Diego Arias†, Jacobo Santamaría, Univ Complutense de Madrid, Dept de Física Aplicada III, Madrid, SPAIN; Carmen Ballesteros, Univ Carlos III de Madrid, Dept de Física, Leganès, SPAIN. †On leave from Universidad del Quindío, Armenia, COLOMBIA.

The structure of high quality [YBa₂Cu₃O₇(YBCO)_N / PrBa₂Cu₃O₇(PBCO)_M] 1000 Å superlattices, with N ranging between 1 and 12 unit cells and M=5 unit cells, grown by high oxygen pressure sputtering, is analyzed by x ray diffraction (XRD) and transmission electron microscopy (TEM). Superlattice structure is refined using the SUPREX 9.0 software¹. The refinement shows epitaxial strain for YBCO thickness below 4 unit cells. Epitaxial mismatch strain results in a surprising reorganization of interatomic distances in the YBCO layers, which correlates with the decrease in the critical temperature². For larger YBCO layer thickness, stress relaxes and step disorder builds up. TEM observations show that the films have the [001] orientation, c-axis orientation, with sharp and flat interfaces between substrate and superlattice stack. The only observable defects are isolated steps or steps associated with regions with [100] orientation, a-axis orientation, not detected by XRD. The results of both structural tools are compared.

¹E.E. Fullerton, I.K. Schuller, H. Vanderstraeten, Y. Bruynseraede, Phys. Rev. B 45,9292 (1992)

²M. Varela, Z. Sefrioui, D. Arias, M. Navacerrada, M. Lucia, M.A. López de la Torre, G. Loos C. León, F. Sánchez-Quesada, and J. Santamaría. Phys. Rev. Lett. (1999)

Acknowledgements: TEM experiments have been done at the Centro de Microscopía Luis Bru. Funds from CICYT MAT94 0604 are also acknowledged.

L9.2

MODELING OF THE TRANSITION FROM ACTIVE TO PASSIVE OXIDATION OF Si(100). Cheol Ho Choi, Mark S. Gordon, Da-Jiang Liu and J.W. Evans, Ames Laboratory, Iowa State University, Ames, IA.

As the temperature is lowered from 1080K to 900K, a transition is observed from active oxidation (etching) to passive oxidation (oxide film growth) of the Si(100) surface when exposed to atomic oxygen [1]. This transition is primarily controlled by the energetics of removal of SiO from the surface. Just below 1080K, an acceleration in surface oxygen buildup may reflect the feature that oxide patches are nucleated (despite the immobility of adsorbed O), and that these are more resistant to thermal decomposition. We develop atomistic models for this cooperative kinetics, which reflect the feature that O-removal from the surface is inhibited for O incorporated into oxide islands. Consequently, these models generalize the so-called contact model from Interacting Particle Systems theory. The modeling utilizes insight into the dependence of the activation barriers for key reaction processes on the local environment, these barriers being obtained from ab-initio quantum chemistry calculations using a large cluster to represent the Si(100) surface.

[1] T. Engel, Surf. Sci. Rep. **18** (1993) 91.

L9.3

MICROSCOPICAL STUDY OF THE NUCLEATION AND GROWTH PROCESS OF SOL-GEL DERIVED BUFFER LAYERS FOR THE INTEGRATION OF YBCO ON BIAXIALLY TEXTURED NICKEL. Harald Dobberstein, Robert Schwartz, Clemson Univ, Dept of Ceramic & Materials Engineering, Clemson, SC; Richard Czerw, Clemson Univ, Dept of Physics and Astronomy, Clemson, SC.

Recently, a promising second generation high temperature superconductor tape product was developed by Oak Ridge National Laboratory. The superconducting tape is fabricated by using a biaxially textured substrate (RABiTS) to promote the epitaxial growth of the buffer layer and YBCO coating. Due to the easy scalability and higher cost efficiency, chemical solution deposition has become an attractive alternative for the fabrication of both the superconductor and buffer layers. In contrast to physical and chemical vapor deposition techniques, where the nucleation and growth process is dictated by surface and interfacial energy considerations, in solution deposition routes, the nucleation and growth characteristics of the layers are also impacted by the difference in free energy between the amorphous and crystalline states. Because of the complexity of this process, the importance of interfacial, kinetic, and thermodynamic factors on the epitaxial growth of sol-gel derived thin films is not yet fully understood. In this presentation, the most influential factors dictating nucleation and growth will be discussed, and emphasis will be given to the initial crystallization stage, as well as to the microstructural evolution of the films. SEM, HRTEM, STM, AFM and X-ray diffraction results will be presented for rare earth oxide and strontium titanate buffer layers on biaxially textured nickel.

L9.4

EPITAXIAL GROWTH OF CeO₂ BUFFER LAYERS ON MgO AND SAPPHIRE SUBSTRATES. A. Thorley, N. Savvides, S. Gnanarajan, A. Katsaros, CSIRO Telecommunications and Industrial Physics, Sydney, AUSTRALIA.

We studied the epitaxial growth of CeO₂ thin films on MgO(100) and r-plane sapphire [Al₂O₃(1102)] substrates. The thin films were deposited at temperatures in the range 650–850°C by dc magnetron sputtering using a cerium metal target. X-ray diffraction techniques (θ -2 θ , pole-figures, ϕ -scans) were used to determine the crystalline quality and texture. All the films showed strong c-axis orientation with minor (111) peaks. For MgO(100) substrates the epitaxial growth of CeO₂ is evident at 650°C, and it develops to almost perfect epitaxy at 850°C to yield (111) pole FWHM $\Delta\phi = 5^\circ$. Epitaxy of CeO₂ onto sapphire appears at higher temperature so that at 850°C the CeO₂ films have $\Delta\phi = 9^\circ$.

L9.5

CRACKING AND DELAMINATION OF HETEROEPITAXIAL BARIUM HEXAFERRITE FILMS. Steven A. Oliver, Center for Electromagnetic Research, Northeastern University, Boston, MA; Izabella Kozulin, Nicol E. McGruer and Carmine Vittoria, Dept. of Electrical and Computer Engineering, Northeastern University, Boston, MA.

Thick highly-oriented hexaferrite films are being considered for nonreciprocal planar devices operating at microwave and millimeter wavelengths. Unfortunately, it has been found that barium hexaferrite films deposited onto the most commonly used substrate, sapphire, often delaminate before reaching a thickness of 15-20 micrometers, presumably due to the large tensile stresses caused by a substantial mismatch in coefficients of thermal expansion. However, a simple model where the film delaminates because of a loss of adherence to the sapphire substrate does not always hold, as micrographs show that this delamination can also occur due to fracture within either the film or substrate. In order to evaluate the magnitude of the thermally induced normal stress within the barium hexaferrite / sapphire system, substrate curvature measurements were made on 1 - 10 micrometer thick films that were deposited by pulsed laser deposition. These films were deposited in oxygen background pressures of either 20 mTorr or 300 mTorr. All films deposited at 300 mTorr showed significant bowing, and no cracking, although the deduced film normal stress was found to decrease roughly linearly with film thickness from 2.5×10^8 Pa to less than 10^8 Pa for films having thicknesses of 1 and 8 micrometers, respectively. For comparison, a stress value of 5.5×10^8 Pa was expected using a biaxial strip model. This stress relief may occur within a highly defective film layer bounding the interface, whose presence has been inferred from magnetometry measurements. In contrast, none of the films deposited at 20 mTorr showed significant bowing, although films having thicknesses above 3 micrometers did possess numerous cracks. This implies that oxygen vacancies may be an important factor for stress relief in the interfacial region for lower pressure films, although the effects of stacking faults may also be significant.

L9.6

FORMATION OF EPITAXIAL FILMS ON THE Ti AND Zr SURFACE IN HYDROGEN PLASMA. Dmitry V. Schur, Mykola Baklanov, Institute of Hydrogen and Solar Energy, Kiev, UKRAINE; Victor B. Voitovich, Vadim M. Adejev, Svetlana Yu. Zaginaichenko, Oleksandr Domashenko, Institute for Problems of Materials Science of NAS, Kiev, UKRAINE; Liliya M. Gerych, Kherson Industrial Institute, Kherson, UKRAINE.

The oxide film is a steady component of metallic titanium and zirconium. The rate of hydrogen transfer through it is one of stages, imposed the limit on the interaction process between monatomic hydrogen and metal, the thin film don't produce a considerable influence on the process of hydrogen adsorption by metal.

Activational barriers are conserved for desorptional flow through the surface film. Thus, film exerts the essential effect on the processes in a volume, bounded by film.

The formation conditions of surface epitaxial films on titanium and zirconium under hydrogen plasma and their influence on the processes of hydrogen phases formation of high pressure at $P=26$ Pa have been examined in this paper. Using Auger scanning spectroscopy and electron probe microanalysis the regularities of the thin surface films formation during Ti and Zr hydrogenation in hydrogen plasma has been studied. Their role in hydrogenation is discussed. It has been ascertained that the oxynitride film on zirconium surface in HFD-plasma is formed in the first moment of hydrogenation and remains unchanged up to the process completion. It is governed by the specimen negative charge as a result of its bombardment with low energy electrons. This potential prevails over oxygen and nitrogen negative potential prevails over oxygen and nitrogen negative potential and prevents from their diffusion into the metal volume. It hinders also from metal cations movement into oxide. The film in this case may grow only when effected by chemical potential. The counterbalancing of potentials leads to the dynamic equilibrium of film growth. This mechanism is valid for the sufficiently thin ($\sim 0,3-1$ μm) oxynitride films. The present mechanism is operated so long as the electrons are capable to overcoming the film barrier. In case of the film thickness exceeding critical one no interaction between atomic hydrogen and metals takes place.