SYMPOSIUM L

Recent Developments in Oxide and Metal Epitaxy—
Theory and Experiment

April 23 – 26, 2000

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*Invited paper
Tutorial

ST. 1: 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 increased 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 r-A technique, in-situ spectroscopic ellipsometry, x-ray photoelectron spectroscopy and angular electron spectroscopy.

Instructors:
Orlando Anciello, Argonne National Laboratory
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SESSION 1.1: GROWTH AND DYNAMICS OF METAL FILMS
Chairs: Shirley Ching and Andreas K. Schmid
Monday Morning, April 24, 2000
Salon 10/11 (Marriott)

8:30 A.M. #1.1
TAILORING EPITAXIAL TEMPLATES FROM REFRACTORY METAL BUFFERS. C.P. Flynn, University of Illinois, Urbana, IL

Refractory metal buffers such as Nb, Ta, or Cr are often used to prevent the growth of polycrystalline films on silicon. The use of epitaxial techniques in this context allows one to tailor the growth of thin film layers on substrates with precise control over crystallographic orientation, stress, and electronic properties. The lecture will begin with an overview of the general approaches to tailoring epitaxial templates using refractory metal buffers. This will be followed by a discussion of the growth of single crystal epitaxial layers on silicon substrates.

9:45 A.M. #1.2
REAL TIME OBSERVATION AND QUANTIFICATION OF DISLOCATION DISSIPATION IN BI-CRYSTALLINE A1 @111, SIMON, W.D. Nix, J. Florando, and O. Leung, Department of Materials Science and Engineering, Stanford University, Stanford, CA; A. Schwantes, 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 nanoindentation, 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 on silicon substrate system. Deposition of aluminum onto silicon at substrate temperatures of 300°C resulted in the formation of a misfit dislocation structure consisting of two variants of A1 (111) (Thomas 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 strains. However, dislocation nucleation and glide is observed to occur along the (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 measurement.
measurements of epitaxial 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 rates. In particular, the population of island pairs at separations smaller than the average follows from depletion in nearby 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 [2]. 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 means-field treatments. I will illustrate several calculations using results from recent Monte Carlo studies [2]. For example, for Co islands on Ru(0001), I show how the rate and direction of capture of additionally deposited Co atoms reflect the local environment of individual islands, as predicted by simulation and rate-equation calculations. Similar observations were reported in the growth of etha pits on Si(100) monitored with LEEM during exposure to oxygen. Here, I also compare exact 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-OSES under contract no. DE-AC03-94AL85000. [1] M.C. Bartelt and J.W. Evans, PRB 54 (1996) R13759. [2] M.C. Bartelt et al., PRB 58 (1998) 1601 & 4676; PRB 59 (1999) 5125.

11:00 AM L1.6
RATE EQUATIONS AND EFFECTIVE CAPTURE NUMBERS. P. Gilmore, C. Rasch, UCLA, Dept. of Mathematics and HRD Laboratories, Malibu, CA; S. Chen, R. Cafisch, UCLA, Dept. of Mathematics; M. Gyure, HRD 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 are for islands of size S is not known. Several approximations for σ 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 incorrect 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 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 show that ripening can also occur by a random exchange of adatoms between islands, without any chemical potential difference. This phenomenon has been observed in a model system: one-dimensional clusters of In on W[110]. Two parallel one-dimensional In chains are prepared on the W[110] surface, which is then heated to 950°C. The fate of individual atoms in the two In 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 surface chain. 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. DEFG02-92ER14130)

11:30 AM L1.8
MODELING OF METAL (100) HOMEOPOLYAXIAL GROWTH AT VERY LOW TEMPERATURES. K.J. Casperson, 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) homeopolyaxial around 100K, where terrace diffusion is imperceptible. 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(100) reveal rougher growth for even lower temperatures around 50K. Motivated in part by recent MD studies, we propose that the interlayer is due to restricted downward funneling where deposited atoms get caught on the sides of nanostructures. Above 50K, certain low-temperature 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, step nanostructures, 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

We develop an island dynamics model that employs the level-set technique to describe epitaxial growth. The surface morphology is described by defining the locations 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. Several 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 mobility of islands as the cause, in particular, a strong deviation in the n-th level. 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 29, 10:00 to 12:00

1:30 PM L2.1
THE EFFECT OF DEPOSITION PRESSURE ON ADSORBATE STRUCTURE AND COVERAGE: OXYGEN ON W[110]. D.E. Muzzall1, C.S. Fadley1,2, and S. Chang1, 2. Department of Physics, University of California, Davis, CA; 3. Materials 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, control the type of oxygen structure present. 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 photoemission spectroscopy and diffraction. We have used ultrahigh vacuum photoemission and Auger microscopy (STM) to examine 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 L1, our studies show that changes in deposition pressure of as little as factor of 3 cause significant changes in the apparent structures, domain sizes (e.g. of [1x2]/O), and the actual resulting coverages at the adsorbate layer in xenon. Low pressure deposition with [1x2]/O for total exposures of 2x10^13 torr causes different yields structures which do not show a distinct LEED pattern, but show small domains, approximately 20x30 A, 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 combination, STM images of the surface resulting from intermediate oxidation (10 min) at medium vacuum pressures of approximately 30 x 10^-5 Pa with adsorbed coverages of 1.5-30% ML. Higher pressure deposition (10^-7 torr) for total exposures of 3 to 6 L yields structures with well-defined LEED patterns (1:2x) and (2:1), 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 of these kinetic mechanisms are in progress. 1. R.X. Yuzvans et al, Surface Science, in press.

1:45 PM #1:2:3 HETEROTAXY: 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 ferroelectricity, 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(III) by in situ ultrahigh 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 heterotaxy to explain the initial oxidation stages of model metal systems. The nucleation and growth of Cu-O2 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, two-dimensional 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 focused on passivation film formation due to oxidation in air at ambient temperature.

The chemical 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 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 MEASUREMENTS. Bert Lüger, Jürgen D. Eibl, Konrad M. Dirschler, 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 rhodium 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 is not known. We have combined this method with a technique to measure ΦRef 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 this technique to both the study of evaporation processes of evaporated thin films of rhodium and follow the oxidation kinetics of rhodium with oxygen exposure. The extended Kelvin Probe method therefore has potential applications as a characterisation tool for thin film epitaxy, particularly engineering applications such as surface science.

3:00 PM L2.4 ATOMIC MECHANISMS OF SURFACE ALLOY FORMATION. Andreas Schmidt, Sandia National Laboratories, Livermore, CA.

Metals that do not form bulk alloys can often produce stable mixed phase films at surfaces. Using photoemission and scanning tunneling microscopy, this talk will highlight some of the most interesting of these surfaces and the atomic mechanisms responsible for their formation and stability. The effect on the magnetic properties of the samples is discussed.
The role of strain in thin film alloy thermodynamics: competition between alloying and dispersion interactions. UC Davis, Dept. of Physics, Davis, CA; Andreas K. Schmid, N.C. Bartelt, V. Oulas, M. Astra, 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 mismatch between the 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 constant stoichiometries are formed. Phase segregation between a pure Ag phase containing dislocations and a pseudomorphic strained Co$_{x}$Ag$_{1-x}$ 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 experiments by measurements of the atomic strain at the interface between the Ag and Co regions in the alloy phase.

Elaboration of single crystalline Au/Ni$_{90}$Fe$_{20}$/Cu/ Ni$_{90}$Fe$_{20}$/Ni(111) spin valves. Antoine Barbier, Christophe Monbaliu, Sophie Bousquet-Guiraud, 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) is of particular interest. We will show that high quality NiO(111) single crystal polar surfaces can be obtained. They are always stabilized by a [012] reconstruction. These surfaces allowed the investigation of the growth of permalloy (Py, Ni$_{90}$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 built on the NiO(111) single crystal behaves like a hard magnetic material because of the interfacial exchange coupling. Growth conditions (time, temperature) and the whole structure (in which the second Py layer is the sensing soft magnetic layer) were determined, giant magnetoresistances (GMR) of 3% at room temperature were observed easily on these structures without optimizing the layers' thickness. 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.

Interfacial energies of metals on oxides by STM: Ag and Cu on 1x1 TiO$_2$(110). S.M. Sutter, M.C. Bartelt, R.Q. Hwang, K.F. McCarty, Sandia National Laboratories, Livermore, CA; D.A. Chemla, Department of Chemistry and Biochemistry, University 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 energy can be determined. Here we demonstrate that scanning tunneling microscopy (STM) has been used to measure interfacial energies of Ag and Cu films on TiO$_2$(110) surfaces. Monolayer coverages (0.1 to 1.3 monolayers) of Ag or Cu were first evaporated on the TiO$_2$(110) substrate at room temperature in ultra-high vacuum (UHV). The surface was then annealed to 850 K 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 would not be obtained under these 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 ~2 J/m$^2$ and ~1 J/m$^2$ respectively [1], and the TiO$_2$(110) substrate has a surface energy of ~0.7 J/m$^2$ [2]. We find unexpectedly low values of 0.5±0.2 J/m$^2$ for Cu/TiO$_2$(110) and 0.5±0.2 J/m$^2$ for Ag/TiO$_2$(110), as compared to other metal-on-oxide systems. These values are close to the predictions from first principles density functional theory (DFT) 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 1x1-TiO$_2$(110).

Atomic layer control of epitaxial Sr$_{0.05}$TiO$_3$, Sr$_{0.1}$TiO$_3$, Sr$_{0.2}$Heterostructures on TiO$_2$-terminated [001] SrTiO$_3$ Substrates by in situ high pressure RHEED. P. Lu, S. C. Pendharkar, Interface Science 2 (1994) 169.

In situ studies of complex oxide growth on oxide substrates. Rodney D. McKee and Mark Yeazell.

The importance of in situ monitors in the preparation of layered oxide heterostructures by reactive MBE. D.G. Schlom, J.H. Hsku, Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA; W. Tian, X.Q. Pan, Department of Materials Science and Engineering, University of Michigan, Ann Arbor; M.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 promises to evolve. 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 growth of SrTiO$_3$, SrBi$_2$Fe$_4$O$_{12}$, Bi$_2$O$_3$, SrTi$_2$O$_7$, PbTiO$_3$, SrTiO$_3$, and Bi$_2$O$_3$ 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 characteristics 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.

Oxidation kinetics during oxide epitaxy studied by an oblique-incidence optical reflectivity difference technique. X.Q. Pan, D. Schlom, M. W. Brown, M. E. Hawley, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM; J. S. Weil, Department of Physics, Davis, CA; Weideng Si, X.X. Xi, Qi Li, Penn State University, Department of Physics, University Park, PA; Qidu Jiang, M.G. Medic, University of Houston, Department of Physics, Houston, TX; Geszchen Yang, Huhua Li, Fan Chen, Zheng-hao Chen, Institute of Physics, Chinese Academy of Sciences (CAS), Beijing, P.R. CHINA.

We studied oxidation kinetics in the epitaxy of SrTiO$_3$, Ln$_2$O$_3$, PbMoO$_4$, SrMoO$_3$, and SrTiO$_3$/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, oxide film composition 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 find that at sufficiently high temperatures, the oxygen in the SrTiO$_3$(001) substrate is mobile enough to move to the surface and oxidize 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.

8:30 AM | 15.3

SESSION L2: IN SITU STUDIES OF COMPLEX OXIDE GROWTH ON OXIDE SUBSTRATES

Chairs: Rodney McKee and Mark Yeazell

Tuesday, April 25, 2000
Salon 10/11 (Marriott)
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 SrRuO$_3$/TiO$_2$ SrRuO$_3$/SrTiO$_3$ heterostructures on perfect TiO$_2$ terminated (001) SrTiO$_3$ substrates using pulsed laser deposition including in-situ high pressure RHEED. SrRuO$_3$ is an ideal system to study the heteroepitaxial growth mechanism of various perovskite thin films and to fabricate high quality multilayered devices. SrRuO$_3$ is a conductive ferromagnetic oxide with a lattice parameter of 3.93Å, i.e., a lattice mismatch with (001) SrTiO$_3$ substrates of 0.64%, AFM studies revealed that the surface morphology of each layers is extremely smooth with a step size 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 SrRuO$_3$ films on SrTiO$_3$ 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 SrRuO$_3$. In contrast, the SrTiO$_3$ films on SrRuO$_3$ grow in the two-dimensional layer-by-layer mode. Such an atomic scale control of the interfaces and barrier layers in ferromagnetic oxide (FM-LFM) trilayer junctions allows for quantitative studies of spin-polarized transport across the ferromagnetic oxide (FM-LFM) trilayer junction interface, which will be discussed.

9:45 AM L3.4

TIME RESOLVED STUDIES OF SrTiO$_3$ HOMOEPITAXY BY SYNCHROTRON X-RAY SURFACE DIFFRACTION


The ability to monitor the evolution of atomic scale surface structure in real-time facilitates the 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 SrTiO$_3$ homoepitaxy by pulsed laser deposition. The intermittent nature of the laser ablation process allows measurement 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=0) and specular (h=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 first principles MD 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

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

10:30 AM L4.1

GROWTH DEPENDENT II-DEPENDENT MAGNETIC DOMAIN STRUCTURES IN La$_{2-x}$Sr$_x$Mn$_3$O$_7$ 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$_{2-x}$Sr$_x$Mn$_3$O$_7$ (LSMO) films by magnetic force microscopy (MFM) for films grown on a compressive [LaAlO$_3$] 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 microstructural and domain structure data. 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 found to be a function of the unit cell volume and 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-domain structures remained even after deprivation of the polarization component returned to the original value. For 800°C the field-dependent magnetic structures were correlated to VSM data. The changes in the magnetic structure correlated directly with the non-linear hysteretic magnetic 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 layer where the domains were pinned in the remanent state.

10:45 AM L4.2

EPITAXIAL TiN OXIDE 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, SrO$_2$ with the rutile structure is widely used as a base material in chemical sensors. In particular, SrO$_2$ thin films have recently drawn much interest because of their potential application in microwave devices. In this report we present our experimental results on the synthesis and characterization of SrO$_2$ epitaxial thin films on sapphire substrates. The SrO$_2$ 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 SrO$_2$/O ratio of the ablation plume, prior to its being mixed with the background 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 structures were investigated by both x-ray diffraction and transmission electron microscopy techniques. It was found that the SnO$_2$ thin films grown on the (10-12) surface of sapphire substrate are epitaxial, single crystal, while those films on the (001) surface of sapphire consist of textured structures with both (110) and (200) oriented grains. The epitaxial growth mechanisms of SrO$_2$ 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 Mg$_2$O BUFFER ON THE EPITAXIAL GROWTH OF ZnO ON Al$_2$O$_3$

Y. Cheon, H.-J. Ko, S-C. Hong, T-K. Hamada and T-S. Yoo, Institute for Materials Research, Tohoku University, Sendai, Japan; J.-N. Yaishuro Segawa, Photon Dynamics Research Center, Institute for Physical and Chemical Research, Senda, 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 high 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 Al$_2$O$_3$ (001) substrate. However, because of the large lattice and thermal mismatch between ZnO films grown on Al$_2$O$_3$ (001) showed poor surface morphology and crystallity. In the present paper, we demonstrate how to improve the surface morphology and crystal quality of ZnO epilayer by using a thin Mg$_2$O buffer. Since Mg$_2$O itself is an II-VI oxide compound, the growth is carried out in the same chamber for growing ZnO without contamination problem. Also there is no additional problem in device design caused by a Mg$_2$O layer, which is completely transparent at the wavelength where ZnO is active as a laser medium. The ZnO films grown on widely used low cost sapphire substrate by plasma assisted molecular beam epitaxy. The thin Mg$_2$O 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, the 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 excitation emissions at 3.3734 eV (Xα) and 3.383 eV (Xβ) are observed in photoluminescence at 4.2 K further indicating the high quality of the resulting ZnO epilayers.

11:30 AM L4.5
DETECTORS AND STRUCTURE OF INTERFACE IN Mg,Zn_{1-x}O/α-Al_{2}O_{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 heterostructure 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, Zn_{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_{x}Zn_{1-x}O and Mg_{x}Zn_{1-x}O:Al alloy films grown on α-Al_{2}O_{3} substrate. These layers were synthesized by pulsed laser deposition using ICF 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 the ZnO epitaxial films grown at the same conditions. It was found a 0.9° 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 defects density with thickness and time of annealing was investigated.

11:45 AM L4.6
EPITAXIAL GROWTH OF Co_{3}O_{4} THIN FILMS BY LOW TEMPERATURE, LOW PRESSURE MOCVD. K. Shalini, Anil U. Mane, R. Lakshmi, S.A. Shivashekar, 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 infusions of high energy through means such as ion bombardment during film growth. We have grown epitaxial thin films of the cubic oxide Co_{3}O_{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 precursor precursor and argon as the carrier gas for the sublimed vapors. When oxygen is used as the reactive gas, polycrystalline films of Co_{3}O_{4} are formed at temperatures ranging from 400-550°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_{3}O_{4} with [100] orientation are formed on single crystal SrTiO_{3}(100). A film grown simultaneously on LaAlO_{3}(100) substrate is also epitaxial, having the [110] orientation. The crystallographic quality of the films (out-of-plane texture and in-plane alignment) was determined by x-ray x-ray diffraction. The films on SrTiO_{3}(100) as grown, show rocking FWHM ~ 0.33 degree, which is comparable to the best values in epitaxial perovskite oxide films grown at similar or higher temperatures of growth. All the wafers of the films on SrTiO_{3}(100) are somewhat larger - 1.65 degrees for as-grown wafers. In an attempt to improve the epitaxial quality, the films were annealed at 725°C in oxygen. The rocking FWHM of the annealed wafers improves to 0.29 degree at SrTiO_{3}(100), and to 1.3 degree at LaAlO_{3}(100). On both these substrates, x-ray 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 proposed for the observed low temperature epitaxy will be proposed.

SESSION L5: IN SITU STUDIES OF OXIDE GROWTH ON SILICON

Chair: Marilyn E. Hawley and Orlando Auciello Tuesday, April 25, 2000
Salamon 10/11 (Marriott)

1:30 PM #L5.1
STUDIES OF FERROELECTRIC THIN FILM GROWTH AND SURFACE PROPERTIES VIA IN SITU ELLIPSOmetry, TIME-OF-FLIGHT ION SCATTERING, AND DIRECT RECOIL SPECTROSCOPY IN WIDE RANGE PRESSURE ENvironments. A.R. Krauss, A.M. DiGio, 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. Mueller, University of North Carolina, 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 (NVRAMs) 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 NVRAMs and high-permittivity DRAMs. When demonstrating 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-ISRARS) and in situ, real-time studies of film growth processes in a wide range of background pressures from high vacuum to tens of millitorrs. TOF-ISRARS 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-ISRARS can monitor the surface composition and structure of thin films, but not buried interfaces. Therefore, we have combined TOF-ISRARS with Spectroscopic Ellipsometry, which permits investigation of buried interfaces as they are being formed. Recent work performed to understand and growth and post-deposition processes and microstructure-property relationships of layered perovskite SrBi_{2}Ta_{2}O_{9} (SBT) and Ba_{1-x}Sr_{x}TiO_{3} (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 polycrystalline metal 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, dynamical processes, in order to reliably obtain the correct film thicknesses. Barrier films will be required which optimize reaction of the complex oxide with a variety of substrates and contact material. On the scientific side the detailed of interface interactions 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 IonWorks 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-ISRARS). Characterization can be performed. A mechanism can be proposed for the observed low temperature epitaxy will be proposed.

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, Ionworks, 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 device performance. Both the proximity and diversity increase the possibility of interdiffusion and for chemical reactions between multilayer thin film materials. Barrier films help to reduce these unwanted interactions. 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 analysis have been performed with ex-situ and/or using destructive techniques, such as Rutherford backscattering spectrometry (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 (MSRI) enables the detection of barrier layer performances for processing conditions. As examples, we will present new results of in-situ studies of the interdiffusion and interaction between Cu/Si with/without a TaSiN 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 6: EPITAXIAL GROWTH OF OXIDES ON SILICON
Chairs: Darrell G. Schlom and Orlando Anciello
Tuesday Afternoon, April 25, 2000
Salon 10/11 (Marriott)

3:15 PM #6.1
STRUCTURE OF THE SILICON-OXIDE INTERFACE. Yuhui Tu and J. Temelli. 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 when compared with real measurements on the interface that provides very accurate representations of the unamorphized 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 #6.2
HETEROEPIFASTY AT AN OXIDE/SEMICONDUCTOR INTERFACE – A CORRELATION BETWEEN PHYSICAL AND ELECTRICAL STRUCTURE. Rodney McKee, Oak Ridge National Laboratory, Oak Ridge, TN.

The fundamental interest in oxide/semiconductor heteroepitaxy primarily reside in development of an understanding of length scale issues. Chemical bonding and crystal symmetry are overriding crystal rules on the lattice mismatch concerning 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 to 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 MAGNETIC OXIDE ON SILICON. F. Niu, B.H. Hoerner 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 metalorganic molecular beam epitaxy using a solid precursor, magnesium beta-aldiketonate and activated oxygen. The process involved the growth of thin epitaxial interlayer followed by deposition of MgO at 800°C. The overlayer was epitaxial with a MgO[001]/Si[011]/MgO[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 infrared 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 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

Oxides with perovskite crystal structure are important candidates for ultra thin gate oxides because of their large DC dielectric constant. When SrTiO3 is deposited on Si, an amorphous non-stoichiometric interface (1.5-3.0A thick) is usually formed during the later stages of growth. This is undesirable, since it reduces the capacitive. Optical tools such as spectroscopic ellipsometry (SE) can easily be adapted for in-line or in-situ diagnosis 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 6.1 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 overaging the amorphous interface and the SrTiO3 film. For film thicknesses between 160 and 200A, n at 633 nm ranges from 2.1 to 2.2 (compared to 2.4 in the bulk). Thinner films [110-130A] have an even lower n around 1.9. We propose that the amorphous interface has a lower index than bulk SrTiO3 and therefore reduces the effective n with decreasing film thickness. For our purpose, 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 TUNNELING EFFECT APPLICATIONS. Jorge Pedro, Hugo Aguayo, Elibia Fortuna, Isabel Ferrera, Rodrigo Martins, New Univ. of Lisbon, Fac. of Science and Technology, Materials Science Dept., CENIMAT and CEMOP/UENNOVA, Monte da Caparica, PORTUGAL.

In the Si/Semiconductor-Insulator-Semiconductor (SIS) solar cells the insulator plays the main role in the device performances. It should be very thin (below 4 nm thickness) and also compact, to form the desired tunneling effect between the two semiconductor layers, the silicon and the semiconductor oxide. The silicon oxide layers must be proposed consists in a two step process. First the silicon wafer is oxidized in a furnace at a temperature of 500°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, are correlated with the data obtained from the X-ray 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 Co-O THIN FILMS WITH [200] PREFERRED ORIENTATION ON Si(100) SUBSTRATE BY RF-MAGNETRON SPUTTERING. Leesung Kim, Jinmo Kim and Dongseung Jung, Dept. of Physics, Sungkyunkwan University, Suwon, SOUTH KOREA.

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

SESSION 18: EPITAXY OF OXIDES AND METALS
Chair: Jeffrey W. Bullard and Bruce W. Wessels
Wednesday Morning, April 26, 2000
Salon 10/11 (Marriott)

10:15 AM L8.1

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 minute-scale technology. 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 that of a superconducting transition by YBa2Cu3O7-y (YBCO) depending upon the exact oxygen content, and the lowering of the dielectric constant of the high K material Bi2Sr2TiO6 (BST) under oxygen deprived conditions. The objective of this study is to examine real-time 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 results YBCO and BST will be presented.

10:30 AM L8.2
Mg GROWN ON MgO(001), (011), AND (111) STUDIED BY RHEED AND STM. Gang Chen, Nan-Ji Chen, Jin-Jin Ku, 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 at all in thin films. 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 morphology during the growth. A polycrystalline structure of 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 c axis packed film is ~ 8 Å. After the film is thicker than 2 nm, it reduces to hcp but with strong orientational dependence. We observe that it is rather straightforward for a fcc (111) switching to a hcp (001) plane because both planes are close packed. On the other hand, fcc (001) and (111) have no corresponding planes in hcp structure. The RHEED intensity of Mg film before stable patterns with fractional order peaks are observed. We believe that it is related to a flat-unit cell, which results from a changing of ABCABC (three units of a fcc structure) to ABAB (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 spiralike, faceted, 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 Wenjiang, Zhou Xing, School of Electrical & Electronic Engineering, Ningyo University, SINGAPORE, Wei Tong, Materials Research Center, Southeast University, Nanning, PR. CHINA.

Bi-Sr-Ca-Cu-O (BSCCO) high Tc superconducting films are deposited on Si(100) substrates with YSZ buffer layers by sputter target of 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 grain 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 1.756. 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 crystallinity of BSCCO films. The analysis of fractal formation mechanism breaks through the unitary diffusion way in DLA and KCA fractal models. This theory is helpful for the improvement of high Tc superconducting films.

11:00 AM L8.4
MICROSTRUCTURE AND PROPERTIES OF PZT[e52], TiO2, AND PZT[100] THIN FILMS DEPOSITED ON TEMPERATE LAYERS. R.E. Korhonen and M.T. Islam**, Energy Technology Division, Argonne National Laboratory, Argonne, IL; G.R. Bui, 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.

Polarized thin PZT[e52], TiO2, and PZT[100] films were deposited at room temperature (450±5°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 Pt/TiO2 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 these 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-31-109Eng38.

11:15 AM L8.5
SOLUTION SYNTHESIS OF EPITAXIAL RARE-EARTH OXIDE THIN FILMS ON ROLL-TEXTURED NICKEL. Jonathan S. Murrell, Zainal B. Vud, University of Tennessee, Knoxville, TN; David B. Beach, Catherine E. Vallet, Mariannas.
L0.3 MICROSCOPICAL STUDY OF THE NUCLEATION AND GROWTH PROCESS OF SOL-GELED DERIVED BUFFER LAYERS FOR THE INTEGRATION OF YBCO ON BIAxially TEXTURED NICKEL. Harald Debelenstein, 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 on biaxially textured substrate (HABIT) to promote the epitaxial growth of the buffer layer and YBCO coating. Due the easy scalability and higher cost efficiency, chemical solution deposition has become an attractive alternative for 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.

L0.4 EPITAXIAL GROWTH OF CeO2 BUFFER LAYERS ON MgO AND SAPPHIRE SUBSTRATES. A. Thorley, N. Sawides, S. Gnanaraj, A. Korvonen, CSIRO Telecommunications and Industrial Physics, Sydney, AUSTRALIA.

We studied the epitaxial growth of CeO2 thin films on MgO[100] and sapphire [Al2O3[0001]] substrates. These thin films are deposited at temperatures in the range 650-850°C by dc magnetron sputtering using a cerium metal target. X-ray diffraction techniques (θ-2θ, pole figures, φ scans) were used to determine the crystalline quality and texture. All films showed strong c-axis orientation with minimal [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 Δθ = 5°. Epitaxy of CeO2 onto sapphire appears at higher temperature so that at 850°C the CeO2 films have Δθ = 8°.

L0.5 CRACKING AND DELAMINATION OF HETEROEPITAXIAL BARUM HEXAFERRITE FILMS. Steven A. Oliver, Center for Electromagnetic Research, Northeastern University, Boston, MA; Izabella Kozulin, Nicol E. McGruder and Carmine Vittoria, Dept. of Electrical and Computer Engineering, Northeastern University, Boston, MA.

Thick highly-oriented hexaferrite films are being considered for non-magnetic 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 delaminates before reaching a thickness of 15-20 micrometers, presumably due to the large tensile stresses caused by the 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 x 10^9 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 x 10^9 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 of the same nanometer cracked. This indicates 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.

The oxide film is a steady component of metallic titanium and zirconium. The rate of hydrogen transfer through it is one of stages, imposing 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 absorption 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 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 (~ 0.34 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.