Thin Films Division
Room 310 - Session TF-ThA
Ex-situ Characterization of Thin Films

Moderator: P. Ruzakowski Athey, PPG Industries Inc.

2:00pm **TF-ThA1 Ex-situ Characterization of Polycrystalline Thin Films***, K. Barmak,* ***J. Rickman,*** Lehigh University **INVITED**

The granular nature of polycrystalline thin films is an increasingly important consideration in modern high technology applications as grain and structural dimensions become comparable. This realization has prompted a renewed interest in understanding those factors which affect the evolution of grain structure in both as-deposited and reacted thin films. This presentation will address the ex-situ characterization of thin films that are of relevance to microelectronics interconnects and magnetic storage media. Experimental evidence from differential scanning calorimetry, x-ray diffraction and transmission electron microscopy studies will be reviewed and details of transformation kinetics and grain structure evolution will be discussed. Theoretical models and computer simulations of these processes will also be presented. Finally, results of algorithm development for automated grain size measurement from transmission electron micrographs will be highlighted.

2:40pm **TF-ThA3 TEM Study of Defects, Domains and Vacancy Ordering in Ga@sub 2@Se@sub 3@/GaAs(100) and Ga@sub 2@Se@sub 3@/Si(111) Thin Films***,* ***Z.R. Dai****, S.R. Chegwidden, S. Meng,* University of Washington*; K. Ueno, A. Koma,* University of Tokyo, Japan*; M.A. Olmstead, F.S. Ohuchi,* University of Washington

Ga@sub2@Se@sub3@ belongs to a class of M2(III)X3(VI) compounds (where M=AL, Ga or In and X=S, Se or Te) that is largely unexplored, but which has potential applications in novel optoelectronic devices. The crystal structure of Ga@sub2@Se@sub3@ is based on tetrahedral atomic coordination as in the zinc-blende structure, but in which one third of Ga sites on the average are left as vacancies to preserve charge balance in the crystal. The existence of vacancies complicates the Ga@sub2@Se@sub3@ crystal structure, with their arrangement leading to a variety of polymorphs and possible defect structures, but the arrangement of vacancies also strongly influences the properties of Ga@sub2@Se@sub3@. In particular, the vacancy ordering in the crystal structure likely results in the unique optical and electronic properties of Ga@sub2@Se@sub3@. In this work, the Ga@sub2@Se@sub3@ films were grown on GaAs(100) and Si(111) substrates, respectively, by Molecular Beam Epitaxy (MBE). The microstructure of the Ga@sub2@Se@sub3@ films were characterized by transmission electron microscopy (TEM). For the case of Ga@sub2@Se@sub3@/GaAs(100), a single crystal Ga@sub2@Se@sub3@ film was obtained, in which a number of plane boundaries parallel to [111] crystal planes were observed, as well as some micro-twins. The electron diffraction analysis indicates that the vacancies are ordered to distribute into the domains separated by the boundaries in some equivalent orientations of the zinc-blende structure. For the case of Ga@sub2@Se@sub3@/Si(111), the Ga@sub2@Se@sub3@ film consists of domains forming a twin relationship each other, relative to the [-110] crystal planes of the Si substrate. The vacancy ordering occurs in the [111] crystal planes and the periodicity of atomic stacking along crystal direction is two times of that for the cubic zinc-blende structure. The ordered arrangement of the vacancies is associated with the surface structure of the substrates. The attribute of the boundaries and formation mechanism of the domains and vacancy ordering will be discussed.

3:00pm **TF-ThA4 Sputtered Deposition of Ni@sub 3@Al Thin Films***, G.B. Thompson, X.D. Zhang, R. Grylls,* ***R. Banerjee****, P.M. Anderson, H.L. Fraser,* Ohio State University

Monolithic Ni@sub 3@Al films have been deposited using a magnetron sputtering technique. Each film was deposited onto an amorphous SiO@sub 2@ substrate at 25°C (unheated), 200°C, and 400°C. X-ray Diffraction, Transmission Electron Microscopy, and High Resolution Electron Microscopy was used to characterize the microstructure of the thin films. A nonequilibrium structure, which can be common in PVD techniques due to the high quench rates from a vapor to solid state, was observed. The phase transition towards the equilibrium state was seen with increased substrate temperature. X-ray diffraction indicated a strong [111] texture to all the deposited films in the growth direction. Although the elevated temperature samples showed the onset of a slight cubic orientation texturing. TEM/HREM was performed upon cross section and plan view specimens. An equiaxed grain structure, with a typical grain size of 20 nm, was seen in the films. No obvious macroscopic grain growth was observed for the elevated temperature samples. However a high density of planar defects was observed in the cross section of the unheated specimen. Formation of these planer defects will be discussed in terms of phase transition and structural stability in the Ni@sub 3@Al thin films.

3:20pm **TF-ThA5 Roughness Measurements With X-Rays Using an Out-Of-Plane Scattering Geometry***,* ***J.J. Kelly IV****, J. Con Foo, J.F. MacKay, M.G. Lagally,* University of Wisconsin, Madison

Surface and interface morphology plays a dominant role in fields ranging from thin-film magnetism to integrated-circuit production. Of the several techniques that can be used routinely for quantitative determination of the surface morphology, diffuse X-ray scattering provides the widest dynamic range in terms of the lateral scale of roughness that can be sampled, from sub-Angstrom to many micrometers. The use of a grazing-incidence geometry enhances surface sensitivity. In investigations to assess the influence of surface and interface roughness in giant-magnetoresistive films, we have measured the diffusely scattered intensity of soft X-rays (~1 keV) from rough surfaces and interfaces of Si, Co, Ni, and their combinations, using a non-conventional approach, an out-of-plane scattering geometry. An out-of-plane measurement is not limited by the shadow edge of the sample surface, and thus it samples a much wider range of reciprocal space and hence a much larger range of roughness wavelengths than a conventional in-plane rocking curve. We use the Born approximation and the distorted wave Born approximation to fit the data. The bandpass of our experiment allows us to extract all the relevant roughness parameters: the mean square roughness @sigma@, the correlation length @xi@, and the roughness exponent h. We have measured a roughness of bare highest-quality polished silicon wafers of less than 0.5 @Ao@, lower than can be measured by AFM or other techniques. Comparisons to rocking curves measured on the same samples in the same chamber will be presented to show the capabilities of this method. Roughness measurements on epitaxial sputter-deposited Co-on-Cu films will also be shown and, as time permits, compared to magnetic properties of these films. This work is supported by AFOSR and NSF. The Synchrotron Radiation Center is supported by the NSF.

3:40pm **TF-ThA6 Accurate Thin Film Density Measured by Energy-Dispersive X-ray Reflectivity***,* ***W.E. Wallace****, W.L. Wu,* National Institute of Standards and Technology

Recent advances in our group in x-ray reflectivity have shown that this technique, applied in the proper fashion, can be a robust and rapid way to measure thin film density on flat substrates. Density is directly related to most thin film properties: dielectric constant, moisture absorption, thermal diffusivity, etc. Until now, measuring the mass density of thin films less than a 1000 nm thick has not been an easy task. Energy-dispersive X-ray reflectivity,@footnote 1@ performed on a modified x-ray powder diffractometer, has been applied to a variety of organic and inorganic thin film materials. The density can be measured to ±1% in a few minutes. Changes in density of a variety of materials have been followed as a function of processing conditions, for example, annealing time and temperature of spin-on-glasses. A description of the technique and some recent representative examples of low dielectric constant materials for ULSI will be given. @FootnoteText@ @footnote 1@W.E. Wallace and W.L. Wu, Applied Physics Letters 67(1995)1203

4:00pm **TF-ThA7 Structure and Electronic Properties of the Novel Semiconductor Alloy Cd@sub 1-x@Cu@sub x@Te***, S. López-López, G. Torres-Delgado,* ***S.J. Jiménez-Sandoval****, O. Jiménez-Sandoval, R. Castanedo-Pérez,* Cinvestav-IPN, Mexico

In this work is presented an investigation of the structural and electronic properties of the novel semiconductor alloy Cd@sub 1-x@Cu@sub x@Te. The samples were prepared as thin films by rf sputtering on substrates made of Corning glass. X-ray diffraction patterns showed that the incorporation of Cu into CdTe did not affect significantly its lattice parameter. The band gap of the alloys measured by optical transmission spectroscopy was smaller than that of pure CdTe by only 50 meV, approximately. Due to its sensitivity to local atomic order, the samples were studied by micro-Raman spectroscopy. The transverse and longitudinal optic modes regularly observed in CdTe were also found in the Cd@sub 1-x@Cu@sub x@Te samples with frequency variations lower than 2 cm@super -1@, and no additional modes were observed. From the Raman experiments it was also determined that the incorporation of Cu precluded the formation of Te aggregates, which are commonly detected in CdTe thin films and bulk samples. The Cd@sub 1-x@Cu@sub x@Te films were p-type and, remarkably, it was found in some cases resistivity reductions by seven orders of magnitude with respect to pure CdTe films grown under the same conditions. This is opposite to the observed behavior on Cu-doped CdTe samples where copper acts detrimentally for electronic transport. Our studies indicated that the samples with the best properties were those in which the copper content was below ca. 7.0 at%.

4:20pm **TF-ThA8 Thickness-Dependence of Infrared Reflection-Absorption Spectra from Thin Film of Anatase-type TiO@sub2@ Grown on Polished MgO(001) Substrate by Ar-ion Beam Sputtering***, D. Osabe, T. Uchitani,* ***K. Maki,*** Yokohama City University, Japan

The structure of thin film of TiO@sub2@ grown on air-cleaved surface of MgO(001) by Ar-ion beam sputtering on a Ti target is controlled by adjusting the partial pressure of O@sub2@ vapour (P@subO@) flowing near the substrate, which has previously been published in J.Vac.Sci. Technol., A, 15, 2485(1997). In the present study we will show that the preferred oriented anatase-type thin film of TiO@sub2@ with its c-axis parallel to the surface is grown on polished MgO(001) substrate held at 550 °C in P@subO@ = 1.1 x 10@super-2@ Pa. The polished substrate was used for studying optical property after X-rays diffraction. The diffraction peak height from the (200) lattice plane of the anatase TiO@sub 2@ film increases sigmoidally with increasing its thickness, d, below 20 nm, and linearly with d above 20 nm. The relationship between infrared reflection-absorption peak height near at 510 cm@super-1@ and d also shows the similar one between the diffraction peak height and d. Some discussion is given how to determine the dielectric function, @epsilon@, as a function of the angular frequency, @omega@, from the infrared reflection-absorption(IR-RAS). @epsilon@(@omega@) is determined by comparing the measured IR-RAS with the calculated one which is performed by evaluating from the Fresnel coefficient for the anisotropic materials on isotropic substrate by adopting the Lorentz model for the dielectric constant. After determining the dielectric function, the ratio of @omega@ for exciting of the longitudinal optical phonon, @omega@@subL@, to the transverse one, @omega@@subT@, that is, so called Lyddane-Sachs-Teller relation, is determined, which equals to the square root of @epsilon@(0)/@epsilon@. For this aim IR-RAS at 100 @<=@ @omega@ @<=@ 1000 cm@super-1@ is required which is shown for rutile-type single crystal of TiO@sub2@. However, IR-RAS at 400 @<=@ @omega@ @<=@ 1000 cm@super-1@ in the present study will be available for judging whether epitaxially-grown thin film is prepared or not and will show that the dielectric property of crystalline regions in thin films of TiO@sub2@ at d > 20 nm are similar to the bulk single crystal.

4:40pm **TF-ThA9 Rutherford Backscattering and Channeling Studies of Al and Mg Diffusion in Iron Oxide Thin Films***,* ***S. Thevuthasan****, W. Jiang, D.E. McCready, S.A. Chambers,* Pacific Northwest National Laboratory*; N.R. Shivaparan, R.J. Smith,* Montana State University

There is growing interest in the epitaxial growth of model oxides on various oxide and metal substrates to obtain high-quality surfaces and films. This interest is being fueled by the utility of these materials in magnetic recording, surface geochemistry, heterogeneous catalysis and integrated microwave devices. A number of single crystal iron oxide films with various stoichiometries and orientations have recently been synthesized in our lab using oxygen-plasma-assisted molecular beam epitaxial growth. In the present work, we have used Rutherford backscattering and channeling techniques to investigate the crystalline quality of epitaxially grown @alpha@-Fe@sub 2@O@sub 3@(0001) on Al@sub 2@O@sub 3@(0001), Fe@sub 3@O@sub 4@(001) on MgO(001), and @gamma@-Fe@sub 2@O@sub 3@(001) on MgO(001). The nature of the film-substrate interface, the crystallographic quality of the films, and Al, Mg, and Fe interdiffusion were investigated. The minimum backscattering yields obtained from channeling and random spectra show that in general the film crystal quality is reasonably good. However, @alpha@-Fe@sub 2@O@sub 3@(0001) grown on Al@sub 2@O@sub 3@(0001) show some disordering at the interface due to the 5.7% lattice mismatch. In contrast, no disorder was seen at the Fe@sub 3@O@sub 4@(001)/MgO(001), and @gamma@-Fe@sub 2@O@sub 3@(001)/MgO(001) interfaces, in keeping with their respective lattice mismatches of -0.36% and -0.89%. Mg appears to outdiffuse into @gamma@-Fe@sub 2@O@sub 3@ film at a lower temperature than that at which Al outdiffusion occurs into epitaxial @alpha@-Fe@sub 2@O@sub 3@. Interestingly, Fe indiffusion was not observed for the @gamma@-Fe@sub 2@O@sub 3@/MgO system until higher temperatures (~800°C) were reached. @FootnoteText@ Work supported by the U.S. Department of Energy, Offices of Basic Energy Sciences and Biological and Environmental Research - Environmental Management Science Program and NSF Grant DMR-9409205

5:00pm **TF-ThA10 Advances in the Characterization of Thin (<30 nm) TiN Films Using SIMS***,* ***A.V. Li-Fatou****, G.R. Mount, V.K.F. Chia,* Charles Evans & Associates

Titanium and titanium nitride films are widely used as barrier stacks to prevent junction spiking. It is also an important material for anti-reflection coatings (ARCs) on aluminum films to facilitate lithography processes during multilevel metallization for the manufacture of integrated circuits on silicon-based semiconductor devices. SIMS (secondary ion mass spectrometry) is a very capable tool for characterizing films because of its excellent detection sensitivities for transition elements and atmospherics. However, as films become thinner (<30 nm) quantitative analysis by SIMS also becomes more challenging. This is because a larger fraction of the film is now located in the transient region of the depth profile where the ion yields are not yet constant. In this paper we describe the effects of various analytical conditions (primary beam energies, incidence angles, and oxygen flooding using quandrupole and magnetic sector mass spectrometers) on the sputter rate at the near-surface and ion yields at the film/substrate interface. The samples used in this study were CVD grown samples of Ti (10 nm) /Si and Ti (3x10 nm)/Si. Our preliminary study shows that oblique angle bombardment with oxygen flooding can result in both accurate quantification and depth calibration in the upper 15 nm of the sample; there appears to be a dependence between the incidence angle and the primary beam energy. Interfacial mixing is reduced by using a lower primary beam energy. Ion yield enhancements are reduced using oblique incidence bombardment and oxygen flooding. Difficulties still exist when using SIMS to determine the exact the film thickness.

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