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In Situ X-Ray Reflectivity Measurements of RECEIVED
Thin Film Structural Evolution NOV 05 1993

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ABSTRACT

X-ray reflectivity using energy dispersive X-ray detection has been used to investigate the characteristics of vacuum deposited thin films. A resolution of 0.3 nm for thickness in the range of 3 - 200 nm and of 0.05 nm for roughness in the range of 0.1 - 3 nm has been demonstrated. Further, it is shown that by using energy dispersive detection, spectra can be obtained in less than 500 s allowing real time studies to be performed. Thin, discrete Cr/Al deposits on quartz substrates have been investigated and the presence of a 1.5 nm thick Al/Cr intermetallic layer formed during room temperature deposition has been determined. During annealing at 250 C, the Cr layer thickness decreases linearly with time until approximately 4 nm is consumed in additional intermetallic formation; further annealing does not change the Cr layer thickness.

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INTRODUCTION

Several technologies presently used or proposed for future products within the electronics and semiconductor industries require the measurement of surface or interface roughness to resolutions of 0.1nm or less. Technologies where the determination of individual layer thickness within multiple layer structures is critical to device performance require similar measurement resolution.

There are several techniques which can probe buried structures, e.g., Rutherford Backscattering (RBS), Transmission Electron Microscopy (TEM), Auger or SIMMS depth profiling, X-ray diffraction (XRD) and ellipsometry. However, ellipsometry analysis is not trivial and requires knowledge of the optical constants for each of the phases present in the film. TEM, Auger and SIMMS depth profiling are destructive of the sample. RBS is limited to ~ 10 nm resolution. And XRD techniques, although potentially sensitive to thin buried structures, cannot easily yield information on the physical extent of these structures. Additionally, all of these techniques (except ellipsometry and XRD) measure samples which are small in area, which makes them difficult to integrate into quality assurance environments.

X-ray Reflectivity (XRR) (1,2) is a technique which can be used to measure large area samples (1cm X 1cm). It can be used as a probe of the top surface for roughness measurements to less than 0.1 nm resolution, and it can be used to determine interface characteristics

for multilayer structures in samples up to ~ 250 nm in total thickness. This technique is complementary to XRD, which is sensitive to the electron density around atoms and yields information on atom lattice structure, and to Energy Dispersive X-ray Spectroscopy (EDX), which samples changes in the electron energies of an atom to provide information on the atom species. Furthermore, unlike RBS, TEM, EDX, Auger or SIMMS, the sample in an XRR measurement does not need to be measured in a vacuum chamber, although a vacuum chamber may be included for sample preparation and environmental control.

It is shown by Als-Nielsen (3) that XRR is sensitive to the gradient in the electron density normal to the surface, dp/dz . Specifically, the reflected intensity is proportional to the squared magnitude of the fourier transform of dp/dz . The electron density gradient is zero where the film composition is uniform, and has peaks at the interfaces between different layers of the film and between the film surface and vacuum. If the composition of the film changes abruptly between layers, then the density gradient will have a sharp peak. If the interface is diffuse, or rough, the composition change will be spread over a larger region and the density gradient will have a broader peak. Interference between scattering from the different interfaces gives rise to oscillations in the reflectivity spectrum. The measured XRR spectrum can therefor be analyzed to obtain the thickness, electron density and interfacial roughness of the individual film layers.

An XRR spectrum is obtained by measuring the ratio of reflected intensity to incident intensity (I_f/I_i) as a function of the scattering vector K ,

$$K = (4 \pi/\lambda)\sin\Theta \quad 1$$

where λ is the x-ray wavelength and Θ is one-half the scattering angle. Replacing λ by

$$\lambda = hc/E \quad 2$$

where c is the speed of light, h is Planck's Constant and E is the x-ray energy yields

$$K = (4 \pi/hc)E\sin\Theta \quad 3$$

In energy-dispersive XRR, a broad range of X-ray wavelengths impinge on the sample at a fixed angle and an energy dispersive Ge detector is used to simultaneously measure the reflectivity at each wavevector k (Figure 1). In comparison, conventional reflectivity measurements are performed at a constant X-ray energy and the scattering angle (2Θ) is varied. The benefits of the energy dispersive technique are a fixed sample position which simplifies in situ measurements and parallel acquisition of all reflected energies which greatly increases the acquisition rate (< 1000 s per spectrum).

For the current experiment, broad-band Bremsstrahlung radiation (5-40 keV) was produced by a rotating anode source operated at 40 kV and 100 mA with a Mo anode. The scattering angle is 1.5 degrees (2θ) and the beam divergence is 0.03 degrees. For analysis, the measured intensities are converted to reflectivity by normalizing the incident energy spectrum and the energy is converted to wavevector using equation 3.

EXPERIMENT

The samples were fabricated by Motorola (Schaumburg) and then shipped and measured at Sandia using the XRR technique. The sample structure consisted of a single crystal quartz substrate (10mm X 10mm x 0.1mm) with a 10 nm Cr layer followed by a 50 nm Al layer (nominal thicknesses). Deposition of the metals was performed using an electron beam furnace in a vacuum of $1\text{E-}6$ torr. Initial XRR spectra were obtained at room temperature to determine the as-prepared structure, and subsequently in vacuo at 250C to measure the evolution of the microstructure during annealing. The XRR measuring time was short (~ 1000 s) relative to the annealing time.

RESULTS AND DISCUSSION

The XRR results for the as prepared sample is shown in Figure 2. The data is represented by the solid line; the spectra are normalized by the Fresnel reflectivity (R_f) for clarity (1). Oscillations in the

spectra are the result of interference between scattering from the multiple interfaces in the structure. Film structure is determined by non-linear least squares fitting to spectra obtained using an optical multilayer theory (2), where the variable parameters are the thickness, electron density and interfacial roughness of each layer. The model calculations are represented in Figure 2 by the dashed lines assuming two different initial structures: a) a 2-layer model assuming an Al/Cr/quartz structure and b) a 3-layer model assuming an Al/intermetallic/Cr/quartz structure. For values of the wavevector greater than 1.7 nm^{-1} , the 2-layer model is clearly inadequate. Adding a thin intermetallic layer between the Al and Cr layers, however, is sufficient to reproduce the observed structure. The sample structure obtained from these parameters is shown schematically in Figure 3; note that the roughness of the Al/vacuum interface (2.77 nm) made it impossible to determine the thickness of the Al layer (nominally 50 nm).

Presence of an intermetallic layer in the as-deposited films has been previously observed using XRD (4); these spectra have revealed the existence of small peaks which can be ascribed to one of several Cr/Al phases ($\text{Al}_{13}\text{Cr}_{12}$, AlCr_2 , or Al_3Cr_5). Intermetallic formation in this system has also been observed by Howard (5). We suspect that the Cr/Al interface identified by XRR is the source of the XRD results which indicate that a Cr/Al intermetallic phase can exist in the as deposited state for this metal system. XRD alone, however, can not determine the thickness of the as deposited layer as XRR can. The electron density of the intermetallic layer is determined from

the fit to be 40% +/- 15% greater than the Al layer electron density. In the as-prepared sample, this layer is well defined, with a roughness of 0.7 nm at the Al/intermetallic interface and 0.98 nm at the intermetallic/Cr interface.

In order to determine the thermal evolution of this structure, measurements were made of the reflectivity during annealing. An initial sequence of anneals at 200 C for a duration of 130 minutes did not produce changes that were large enough to be easily measured, so the annealing temperature was raised to 250 C. A series of spectra showing the evolution of the structure during annealing at 250 C is shown in Figure 4 with the fitted spectra superimposed; the duration of the anneal is indicated on the figure.

Several features of the structural changes are evident in the data. The increase in the period of the oscillations in k-space is caused by a decrease in the thickness of the Cr layer. In Figure 5, the Cr layer thickness is shown to decrease linearly in time until approximately 250 minutes have elapsed, when the decrease stops. Subsequent annealing up to 580 minutes (not shown) did not change the thickness of the Cr layer further. The decrease in the intensity of the oscillations in Figure 4 is caused by an increase in the diffuseness or roughness of the interface between the Cr and the intermetallic layer during the course of the thermal anneal. It is clear from the fitting results that the Cr/quartz interface roughness does not change during the annealing at 250 C. The evolution of the width of the Cr/intermetallic interface is shown in Figure 6. The

interface roughness is observed to increase with a square root of time dependence, suggesting that the interface growth may be governed by a diffusion process.

A second Al/Cr/quartz sample (same metallization thickness) was annealed at 300 C and XRR measurements were performed similarly to the 250 C anneal (data not shown). Behavior similar to that shown in Figure 4 was observed. The two thermal anneals indicate that the interface may be growing by consuming the Cr metal, until such time that the Al cannot diffuse through the resulting interface. When this situation is reached, the Cr thickness no longer changes. Increased annealing temperature would be expected to result in increased diffusion and a further decrease of the Cr thickness. The fact that the Cr/Al interface does not change as rapidly as does the Cr thickness may be related to the different density and volumes between the newly developing intermetallic phase and the Cr. The stoichiometries of the proposed intermetallic phases do not result in strict one-to-one replacements for the unit cell structures with elemental Cr.

CONCLUSIONS

The XRR technique has been used to investigate multi-component thin films. The technique reveals information on the relative thicknesses of the deposited films, the surface roughness of the outermost deposited material and the width of the innermost

interface. For the metal system investigated here, evidence for a Cr/Al intermetallic existing at the elemental interface was revealed. Annealing this system at 250 C revealed the increase in the width of the Cr/Al interface to be proportional to $t^{1/2}$. Furthermore, a decrease in the Cr layer thickness was observed which varied linearly with time.

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Figure Captions:

Figure 1. Schematic of X-ray reflectometer (XRR) using energy dispersive detection.

Figure 2. XRR spectra with experimental data and model. The model assuming 3-layers exist in the sample provides a better fit to the data than does the model assuming a 2-layer fit.

Figure 3. As-prepared sample structure determined from the XRR results.

Figure 4. Evolution of the XRR spectra for a Cr/Al sample as a function of annealing time at 250 C. The first maxima shown shifts towards increased K with annealing time.

Figure 5. Change in Cr layer thickness as a function of annealing time at 250 C.

Figure 6. Change in Cr/intermetallic interface width as a function of annealing time at 250 C.

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