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Physica B 336 (2003) 145–150
PHYSICA B
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Oxygen-assisted growth of Co/Cu multilayers investigated with X-ray scattering

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Received 26 September 2002; accepted 28 January 2003

Abstract

Surfactants—surface additives which change surface kinetics—provide a useful additional tool for controlling the growth of thin films. A long history of work on the field has produced a sometimes conflicting view of what surfactants do, and little information exists in the particular field on non-epitaxial multilayer films. Using specular and diffuse X-ray scattering, we examine the effects of oxygen as a surfactant on multilayer Co/Cu films, and find that oxygen improves the layer-to-layer roughness correlation, while also smoothing the layers. Oxygen used at a constant background pressure of 10^{-8} Torr has the best structural properties.

Keywords: Surfactant; Multilayer; Cobalt; Copper; Diffraction; Diffuse; Scattering

1. Introduction

With the ever-rising demands on thin film technology, understanding and controlling thin film growth is increasingly important. In the particular case of giant magnetoresistive (GMR) sensors, the strength of the antiferromagnetic coupling is dependent on the interfacial structure, which in turn depends on the growth of the material. Surfactants—a term given to useful surface contaminants—have been shown to improve GMR devices [1–3] by somehow altering the growth mode [2,4–6,3,7–10]. In particular, a small background concentration of oxygen has been shown to improve magnetic performance of GMR devices. These improvements can be linked both to changes in morphology (roughness, intermixing, and pinhole density) as well as changes to scattering due to oxygen defects. A better understanding of the structural changes will allow modelers to better separate the transport effects of oxygen inclusions from the physical changes. More importantly, success and understanding in these simple structures will improve our ability to engineer more complex nanostructures.

X-ray scattering has been widely used to determine the structure of buried interfaces, including the correlation of interfaces. The majority of results and theory [11–14] on diffuse scattering from "rough" films are confined to systems with low root mean square roughness, high Z contrast, and large in-plane correlation lengths. In contrast, the Co/Cu system shows low

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0921-4526/03/$ - see front matter © 2003 Published by Elsevier Science B.V.
doi:10.1016/S0921-4526(03)00283-7

Z contrast, high roughness, and short correlation lengths—all of which make unambiguous structure determination difficult [15,16].

In this article, we report on the observation and characterization of magnetron-sputtered Co/Cu multilayers deposited under the presence of a variety of surfactants, including oxygen, silver, and lead. Though the materials are immiscible, the large difference in surface mobilities and energies contribute to kinetic intermixing and pinhole formation. The addition of very small amounts of oxygen appears to suppress this behavior. At very high oxygen partial pressures, the oxygen tends to create rougher films.

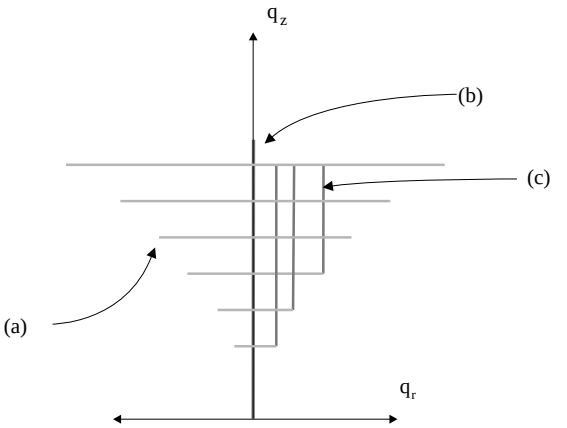

Fig. 1. Path of scans in current experiments. Path (a) is a q_x scan, path (b) is the specular scan along q_z. Path (c) shows offset scans, parallel to the specular direction.

2. Experimental techniques

Co/Cu multilayers were deposited in a DC magnetron sputtering system with a base pressure of $\leqslant 5\times10^{-9}$ Torr with Ar sputtering pressure of 3 mT. The deposition rates as measured by crystal rate monitor was approximately 1 Å/s. For the studies of surfactant materials, multilayers were grown with 20 Å thick layers of Co, and Cu thickness varied around the second GMR peak of approximately 22 Å. For the studies with oxygen, varying partial pressures between 10^{-9} and 10^{-6} Torr of O_2 were used. Additionally, we "puffe" 10 Langmuirs of oxygen on the Co or Cu interfaces during multilayer growth.

Small-angle reflectivity measurements were performed on the focused wiggler diffraction beamline, BL 7-2, at the Stanford Synchrotron Radiation Laboratory (SSRL). X-rays of energy 8037 or 8937 eV (depending on experiment), monochromatized by a Si(1 1 1) double crystal, were focused to a spot size of 1.0×1.0 mm. One mrad Soller slits were used to define the diffracted beam. Three types of scans were conducted: specular $\theta-2\theta(q_z)$ reflectivity scans, transverse q_r-scans in which only the transverse component of the scattering vector varies, and offset q_z scans, with the reciprocal space direction parallel to a $\theta-2\theta$ scan, but offset by some amount in q_r (Fig. 1).

An energy-sensitive detector was used, with an energy resolution of approximately 200 eV. The Co fluorescence signal was monitored in tandem with the elastic signal. The fluorescence signal was spline fit and used as a beam area normalization. This proved to be an important addition to the experiment, and greatly improved error levels.

3. Results and discussion

Symmetric scans of the multilayers were fit with an optical model ([17] and the references therein) to determine the total (correlated and uncorrelated) roughness. The existence of finite thickness fringes provides an approximate indicator of the degree of total roughness in the film, while the off symmetric scans in the q_z direction show the degree of *vertical* roughness correlation.

In the X-ray scans shown in Fig. 2, the addition of oxygen clearly increases the finite thickness oscillations, as well as increasing the strength of the bilayer peaks. The increased extent of finite thickness oscillations points out an increase in the smoothness of the top layer, while the increased extent of bilayer peaks is most likely due to sharper Co/Cu interfaces, or equivalently, smoother interfaces.

Quantifying the degree of roughness correlation requires looking at the diffuse scattering. Scans made in the q_z direction offset slightly in q_r show

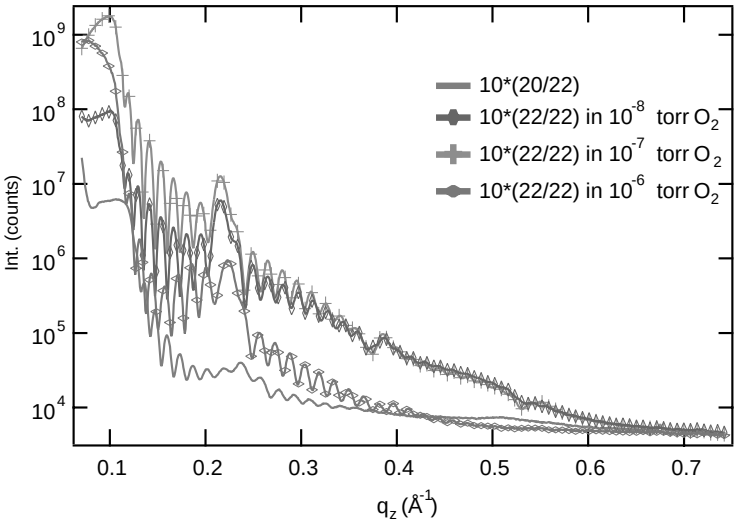

Fig. 2. q_z scans from films grown under various oxygen partial pressures. Increasing O_2 partial pressure improves the film smoothness, as seen from the extent of the finite thickness oscillations.

the diffuse scattering resulting from correlated interfaces. For fully uncorrelated interfaces, the diffuse scattering along the q_z direction is featureless and much lower in intensity than the specular scattering. For fully correlated interfacial roughness, the diffuse scattering is an exponentially modulated copy of the specular scattering.

The replication of finite thickness oscillations in the offset scans is indicative of the increased layer to layer correlation of the roughness of the films. The total roughness is decreased for the film grown in the presence of a slight background partial pressure of oxygen. Figs. 3 and 4 show the results from oxygen surface doping experiments. Adding oxygen to just the Cu surface clearly roughens the film (the films are entirely equivalent other than the method of oxygen addition).

This marked difference in roughening behavior is also seen in the diffuse scattering measured in plane (k-scan). The rocking curves measured at the q_z position of the Bragg peaks from the multilayer are dependent on the sum of the correlated and uncorrelated roughness. Between the Bragg peaks, there is only a dependence on the uncorrelated roughness. Consequently, fitting the diffuse scattering on and off Bragg peaks allows us to distinguish the correlated and uncorrelated roughness. We chose a relatively simple in-plane correlation function with an analytic Fourier transform given by [13]

$$I_{\mathrm{diff}}(q_z, q_x) = \rho^2 \frac{\mathrm{e}^{-q_z^2\sigma^2}}{q_z^2} \sum_{m=1}^{\mathrm{inf}} \frac{\xi(q_z^2\sigma^2)^m}{m(m!)} \times \left(\frac{m^2}{m^2 + q_x^2\xi^2}\right). \quad (1)$$

This equation converges quickly for $\sigma q_z \leqslant 1$. We fit by taking the first 50 terms in the series, which is convergent for $\sigma q_z \leqslant 5$. The scans here are q_r scans, corrected for absorption and sample area illumination. A closer look at the fit function shows that the fitted parameters are all functions of q_z to an even power. A good rule of thumb for data, then, is that samples showing no curvature, or curvature only beyond the Yoneda wings, cannot be unambiguously fit. We follow the method outlined by Savage [12], looking at the diffuse scattering on and off the multilayer Bragg peak. If the roughness is highly correlated, there will be a different curvature to q_x scans on and off the Bragg position.

From Fig. 5 the fit of the diffuse scattering shows the roughness and in-plane correlation

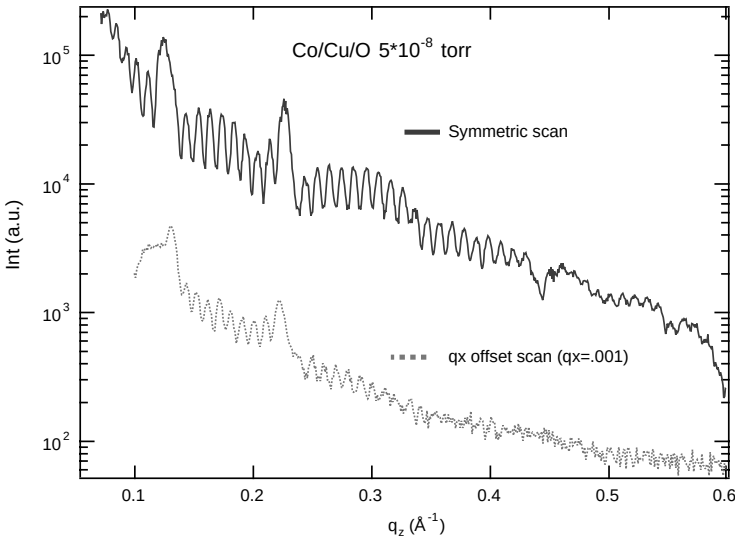

Fig. 3. The replication of specular feature data in the off-specular data shows the correlation of the layers.

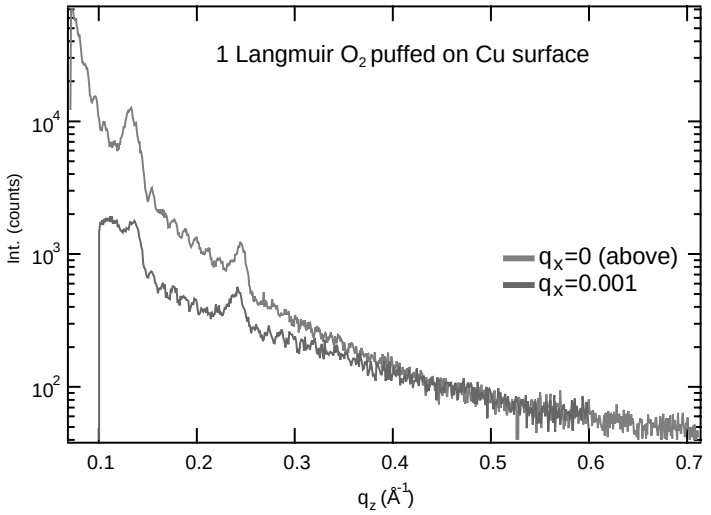

Fig. 4. Adding oxygen only to between the layers creates fairly rough films, with interlayer roughnesses of over 7 Å r.m.s.

length. The quantity of interest is the difference between the square of the roughnesses measured on and off the Bragg peak. This difference is also far more statistically robust than the absolute roughness measured. In Fig. 5, this difference is 4.7 Å. This is the correlated roughness. A more intuitive and useful means of representing this is to use a ratio of the squares of the correlated roughness to the total roughness. This presents a useful correlation coefficient for the multilayer.

From a variety of experiments, we can determine the following:

The results from all the roughness fits show a very narrow range of useful surfactant actions, as measured by diffraction though the films grown with a partial pressure of 10^{-7} Torr are too rough

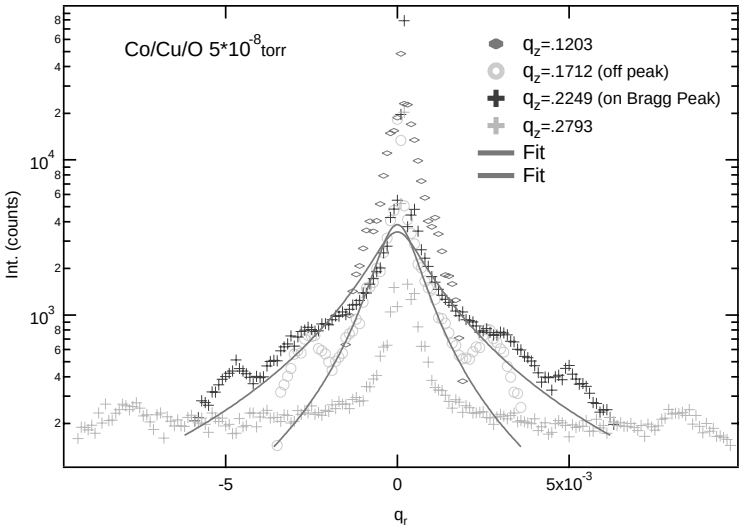

Fig. 5. Diffuse scattering data and fit from film grown with a partial pressure of 5×10^{-8} Torr O_2. All sections are fit at the same time, with roughness allowed to vary between the traces taken at different q_z positions.

Table 1
Various fit parameters from surfactant-assisted growth are compared

Sample (best case)	σ_{tot}	σ_{c+u}	σ_{corr}	$\sigma_{corr}/\sigma_{tot}$	ξ	Stability
Co/Cu $20 \times (30/23)$	6.1	5.8	?	?	250	no
Co/Cu $20 \times (15/23)$	6.0	8.9	6.8	0.7	450	yes
Co/Cu/O $P_{O_2} = 5 \times 10^{-8}$ Torr	4.8	6.4	6.1	0.9	1400	yes
Co/Cu/O $P_{O_2} = 1 \times 10^{-8}$ Torr*	4.8	6.4	5.5	0.8	1400	yes
Co/Cu/O 1 Langmuir per interface	6.8	6.4	5.5	0.8	NA	yes

All numbers are in Å.

to measure. The differences in the in-plane correlation length are reflective of a change in growth mode, but not physically meaningful in this case.

For the films grown with oxygen "puffed" onto either the cobalt or copper surface, there is very little difference from the films grown without any oxygen (Table 1).

The most likely explanation is that oxygen changes the growth mode of the film, but not the initial nucleation of each layer. One caveat to this explanation is that the delay inherent in doping the surfaces with oxygen may cause another effect, and as such, we cannot entirely rule out an interfacial effect for oxygen. However, the most likely explanation is still that oxygen changes growth mode by altering some surface diffusion barrier.

This is consistent with literature results showing a change in surface reconstruction upon addition of oxygen. This reconstruction may have an effect even in the polycrystalline, high deposition rate films studied here.

4. Conclusion

Using low-angle X-ray scattering, we are able to show that the use of oxygen in magnetron sputtering systems smoothes films, as well as increases the layer-to-layer correlation. This increased correlation is coupled with an increased lateral correlation length; in addition, dosing the top of each successive multilayer component made for rougher films, while dosing the surfaces, while also having a background partial pressure

improved the films. The clear implication for a single-layer film would be an enhanced diffusivity. In the case of a multilayer, that is not necessarily true, though it is certainly a possibility. Given the dosing results, there is only a minor effect on the nucleation.

This effect may be due to the decreased diffusivity of the Cu in the presence of oxygen. Decreased interlayer transport would tend to decrease the very high frequency roughness associated with intermixing. Thus, the average correlation length would increase, even in the presence of a small decrease in diffusivity. Eventually, the low diffusivity will lead to excessive defects in the microstructure, explaining the initial improvement in multilayer properties, and eventual decay at higher oxygen partial pressures.

Uncited references

[18–23].

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