ION BEAM MIXING AND THERMAL DEMIXING OF Co/Cu MULTILAYERS

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ABSTRACT

X-ray reflectivity and magnetotransport studies have been used to probe the effects of ion-beam irradiation and subsequent thermal annealing on the structure and giant magnetoresistance (GMR) in Co/Cu multilayers. Low-dose ion bombardment produces interfacial mixing which is accompanied by a systematic suppression of the antiferromagnetic (AF) coupling and the GMR. For ion doses not exceeding 5×10^{14} ions/cm^2, subsequent thermal annealing restores the abrupt interlayer structure as well as the GMR. The combination of low-dose ion bombardment and thermal annealing provides an *ex situ* technique to modify interface structure *reversibly* over a gnificant range.

'TRODUCTION

Artificially layered materials of alternating ferromagnetic and non-magnetic materials have generated considerable interest due to their unique magnetic and transport properties such as GMR and interlayer AF coupling [1]. In this context, interfacial structure plays a crucial role so that it is necessary to establish a technique capable of modifying interface structure in a systematic way. Using a co-deposition technique, Susuki *et al.* [2] reported that the MR in Co/Cu was weakened by artificial intermixing and thus concluded that the scattering centers causing the GMR were in the Co layers. However, co-deposition, like other *in-situ* techniques aimed at modifying interfaces, also affects the growth of subsequent layers and therefore the crystallography of a film. Moreover, direct comparison between different samples is often inconclusive. Post-growth thermal annealing has proven very successful in clarifying the role of intermixing in Fe/Cr [3] but has little measureable effect on the interface structure in Co/Cu [4], in part, because of the very limited equilibrium solubility of Co in Cu.

Recent studies [5,6] have demonstrated that ion-beam irradiation is a promising technique for modifying interfaces. In this paper, we report x-ray reflectivity and magnetotransport measurements on ion bombarded and annealed Co/Cu multilayers. By controlling ion dose, the interlayer magnetic coupling and the GMR can be varied systematically in a *single* sample. As a result of the strong immiscibility between Cu and Co, it is found that the metastable ion mixing can be largely reversed by thermal annealing following the irradiation. Taken together, the structural and transport data demonstrate that the ion bombardment is capable of generating a systematic intermixing at the interface and that the GMR in Co/Cu is very sensitive to such a process.

EXPERIMENTAL DETAILS

Multilayers with the configuration Cu(50 Å)/[Co(17 Å)/Cu(t Å)]$_{30}$ with t = 22 and 34 Å were prepared by rf triode sputtering onto glass (Corning 7059) substrates at deposition rates of 2 Å/s for Cu and 1 Å/s for Co [7]. With these Cu thicknesses, the multilayers are situated at the second and third peaks of the GMR oscillation. Nominal thicknesses were confirmed by surface profilometry and low-angle x-ray reflectivity measurements. Sample magnetization was measured at room temperature using a vibrating sample magnetometer and transport measurements were made, also at room temperature, with a high-resolution ac bridge. The

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sample structure was characterized by low- and high-angle x-ray scattering techniques using Cu K_α radiation.

Ion-beam irradiation experiments were performed in a vacuum of 10^{-7} Torr with 1 MeV Si^+ ions at currents below 50 nA/cm^2. To limit heating effects during irradiation, the samples were placed in thermal contact with a copper block kept at 77 K. Irradiation doses ranged from 10^{12} to 5×10^{14} ions/cm^2 which resulted in about 0.001 to 0.5 displacements per atom as estimated by TRIM simulations [8]. The energy loss of the 1 MeV Si^+ ions in the 1000 Å thick sample is less than 200 keV so that only a small fraction (< 0.1%) of the implanted ions come to rest in the multilayer. Some of the irradiated multilayers were also annealed in vacuum up to 325 °C.

RESULTS

Structural Properties

Fig. 1 presents low-angle x-ray spectra of a [Co(17 Å)/Cu(34 Å)]$_{30}$ multilayer, (a) as-deposited, (b) after irradiation with a dose of 2×10^{14} ions/cm^2 and (c) after subsequent anneal for four hours at 250 °C. The as-deposited multilayer shows clear first- and second-order superlattice peaks, which confirm that the Co/Cu interfaces of the multilayer are well-defined. After irradiation, two superlattice peaks are also observed although their intensities are reduced. Given the fact that the reduction in specular superlattice peak intensity is an indication of increased interface roughness in a multilayer structure, the principal effect of the low dose irradiation has been to disorder the interfacial region.

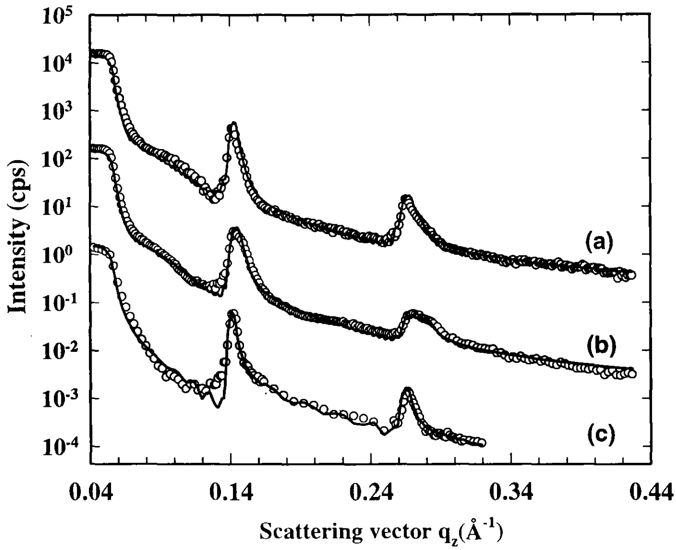

Figure 1. Low-angle x-ray reflectivity spectra for a [Co(17 Å)/ Cu(34 Å)]$_{30}$ multilayer: (a) as-deposited, (b) after irradiation at 2×10^{14} ions/cm^2 and (c) after annealing at 250°C for 4 hours. The solid lines are fitted curves as described in the text. Curves (b) and (c) have been displaced for clarity.

To quantify the effect of the ion bombardment, the x-ray spectra have been fitted with a standard optical model [7] in which the x-ray reflectivity is calculated using a matrix method. A global interface roughness factor has been incorporated into the calculation by assuming a Gaussian form (with a Debye-Waller factor $\exp(-\sigma_r^2 q_z^2)$ where, σ_r is the root-mean-square roughness). In addition, layer thickness fluctuations and film surface oxidization are included to calculate the background intensity profile. The resulting fitted curves for all the spectra have been superimposed on the experimental spectra in Fig. 1. For the as-deposited multilayer, an interface roughness of 5.7 ± 0.5 Å has been calculated.

For the irradiated multilayers, the intermixing induced by ion irradiation is simulated in the calculation by introducing two extra layers at each interface, which correspond to a Co-rich region ($Co_{1-x}Cu_x$, where x<0.5) and a Cu-rich region ($Cu_{1-x}Co_x$, where x<0.5) respectively. Taking advantage of the fact that the x-ray reflectivity is measured on a single multilayer sample before and after irradiation, other parameters, such as the layer-thickness and roughness are kept fixed. Fig.1(b) shows the fitted curve for the multilayer after irradiation at a dose of 2×10^{14} ions/cm^2. The best fit to the data yields x=0.1 and a mixing width of about 11 Å but these parameters are highly correlated. For fixed x in the range from 0.05 to 0.3, (which is comparable to the mean number of displacements at this ion fluence), the intermixing width varies from 6 to 12 Å, all of which are small compared with the wave-length of the multilayer. This analysis leads us to conclude that the principal structural effect of the irradiation has been to blur the Cu/Co interface over a range of approximately 10 Å without significantly altering the periodic structure of the multilayer.

This point is reinforced by considering the cascade mixing width Ω of the beam [9]

$$\Omega^2 = \frac{1}{3}\Gamma_o \frac{F_D}{N}\xi_{21}\frac{R_c^2}{E_c}\Phi \quad , \qquad (1)$$

where $\Gamma_o = 0.608$, N is the atomic density, $\xi_{21} = [4M_1M_2/(M_1+M_2)^2]^{1/2}$ (M_1 and M_2 are the masses of the atoms involved in the collision), F_D, the energy deposited per unit length due to nuclear collisions, E_c, a threshold displacement energy , R_c^2, the mean-square range associated with E_c, and Φ, the ion dose. Taking typical values of E_c = 25 eV, R_c = 10 Å, and F_D = 35 eV/Å [8], eq(1) predicts a dose of order 10^{16} to 10^{17} ions/cm^2 to reach a mixing width comparable to the wave-length of our multilayers. Our dose levels are 2 orders of magnitude smaller than these, so that eq(1) predicts a cascade mixing width of about 5 Å in line with the value of the mixing width from the x-ray analysis.

High-angle x-ray diffraction after each sample treatment reveals little change in crystallographic structure. Multilayers are textured principally in the fcc (111) direction with a relatively weak fcc (200) component. Using the Scherrer formula, we estimate a length scale normal to the surface of about 130 Å which is much larger than the individual layer thicknesses, and suggests good structural coherence across the interfaces. For ion doses less than 5×10^{14} ions/cm^2, it is found that the linewidth of the (111) Bragg peak is nearly unchanged upon irradiation, indicating the structural coherence length is not strongly influenced. As well, a small increase in the relative intensity of the (200) peak is observed.

Annealing effects on the irradiated multilayers are of particular interest. Fig. 1(c) shows that the intensities and the linewidths of the superlattice peaks have fully recovered after annealing. In contrast, x-ray reflectivity spectra of virgin Cu/Co multilayers are little affected by annealing at the same temperature [4]. Due to the equilibrium immiscibility of Cu and Co, annealing at moderate temperatures provoques a back-diffusion from the metastably mixed regions and the reformation of relatively abrupt interfaces. This spectrum can be fitted without the interfacial layers introduced for spectrum 1(b), with a slight increase of the interfacial roughness to 6.5 ± 0.3 Å.

Magnetotransport Measurements

Ion-beam mixing and demixing suggested by the x-ray analysis can be further evidenced from the resistivity and magnetoresistivity measurements. For ion-beam doses up to 10^{13} ions/cm^2, no change in the electrical resistivity of the multilayers is observed. Above this fluence, the saturation resistivity (ρ_s) of a multilayer increases progressively as a function of total ion dose. A dose of 5×10^{14} ions/cm^2 results in a 60% increase in ρ_s [5]; in contrast, the resistivities of 1000 Å Cu and Co films are nearly unchanged for this dose. Since in these multilayers the electron mean free path is comparable to the layer thickness, the increase in resistivities can be directly connected with enhanced electron scattering as a result of ion-beam mixing across interfaces.

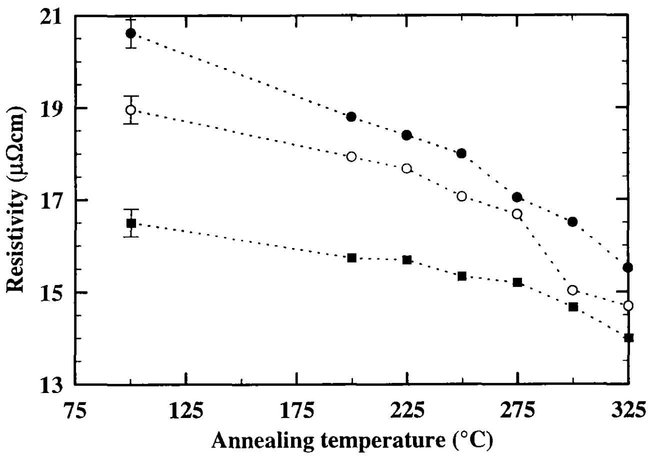

Figure 2. Resistivity versus annealing temperature for three [Co(17 Å)/Cu(22 Å)]$_{30}$ multilayers: as-deposited (■), irradiated at 1.3×10^{14} ion/cm^2 (O) and at 2.6×10^{14} ions/cm^2 (●).

Fig. 2 shows the variations in resistivity upon thermal annealing for three nearly-identical [Co(17 Å)/Cu(22 Å)]$_{30}$ multilayers. Two of the multilayers were subjected to irradiations at 1.3×10^{14} and 2.6×10^{14} ions/cm^2 before annealing for periods of four hours at temperatures below 250 °C and two hours at higher temperatures. As shown in the figure, the resistivities of the irradiated multilayers decrease dramatically upon subsequent annealing. The resistivity of the non-irradiated multilayer also decreased but to a much smaller extent; this decrease is probably related to minor grain growth during annealing. Nevertheless, Fig. 2 demonstrates that the resistivities of the multilayers irradiated at various doses are getting very close to that of the non-irradiated sample, suggesting significant demixing occurs on heating.

Fig 3(a) shows that the GMR falls monotonically with ion dose for the multilayers [Co(17 Å)/Cu(22 Å)]$_{30}$ (at the second GMR peak) and [Co(17 Å)/Cu(34 Å)]$_{30}$ (at the third GMR peak). Given the fact that the GMR is interface related, it is a clear indication that these ion doses produce significant interface modification. It is interesting to note that in Fe/Cr multilayers, Kelly *et al* [6] found that ion irradiation led to an increase in the GMR in spite of a significantly reduced AF coupling. Such behaviour was explained in terms of the enhanced spin-dependent electron scattering at the Fe/Cr interfaces. In contrast, we observe no increase in the MR (either in $\Delta\rho$ or $\Delta\rho/\rho_s$) upon irradiation in any of our Co/Cu multilayers at any dosage level. This behaviour suggests that the role of interface scattering in the GMR might be quite different for Co/Cu and Fe/Cr multilayers.

In the process of interfacial demixing by annealing, the GMR increases sharply, as shown in Fig. 3(b); also shown is the minor increase in MR for the as-deposited sample. The slight increase in the MR ratio for this sample is the result of the decrease in the resistivity related to grain growth. The much more significant rise in the MR of the irradiated multilayers is, however, due mostly to the increase in $\Delta\rho$ (the field induced change in the resistivity) and is more likely to be associated with the demixing process. The MR of the multilayer irradiated at the higher dose increases nearly a factor of three from about 4% to about 12% upon annealing at 200 °C for four hours. Also, the MR of the multilayer irradiated at the lower dose has fully recovered to the as-deposited value after annealing at 250 °C. When annealing temperatures are increased above 300 °C, the MR starts to decrease for all the multilayers, as the multilayer structure begins to break down. However, at each annealing step below this temperature, the MR of all multilayers irradiated at doses < 5×10^{14} ions/cm^2 systematically increase. This increase in GMR is accompanied by an improvement in the AF coupling between Co layers.

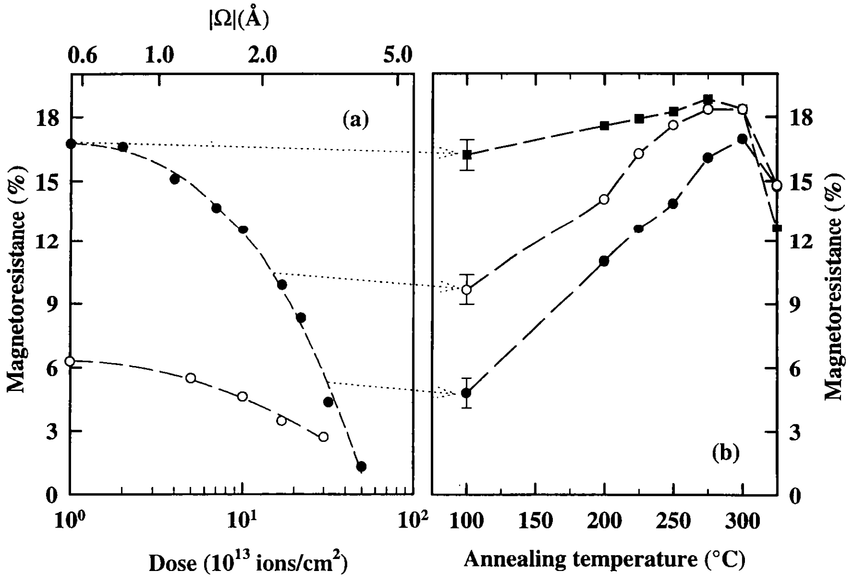

Figure 3 (a) Magnetoresistance as a function of ion dose for [Co(17 Å)/Cu(22 Å)]$_{30}$ (●) and [Co(17 Å)/Cu(34 Å)]$_{30}$ (O) multilayers. The Ω scale at the top of the figure has been calculated using eq.(1). (b) Variations in the GMR with annealing temperature for three [Co(17 Å)/Cu(22 Å)]$_{30}$ multilayers subjected to ion doses of 0 (■), 1.3×10^{14} (O) and 2.6×10^{14} (●) ions/cm^2, respectively.

There are two principal ways in which the GMR can be modified by interfacial mixing: the introduction of additional electron scattering centers with scattering asymmetry different from other mechanisms, a direct effect on the GMR; or the modification of the interlayer magnetic coupling, an indirect effect. For the latter, a first-principles calculation [10] demonstrates that a small amount of interdiffusion at the interface can dramatically suppress the AF coupling due to strong disorder between Cu and down-spin Co states. This situation is expected to be applicable to the Co-Cu interface after ion-beam mixing. An analysis of magnetization data indicates that the AF coupling is systematically reduced by irradiation, a result which is qualitatively consistent with the calculation [10]. In contrast, annealing of the irradiated multilayers always leads to an improvement of the AF coupling. This variation can be explained by the back-diffusion upon annealing which produces a sharper and more atomically-ordered interface region.

CONCLUSIONS

Ion-beam irradiation at low doses provides a means of intermixing and roughening interfaces between metallic layers of multilayer samples. In the case of the Co/Cu films studied here, the AF interlayer coupling and the GMR can be reversibly altered *ex situ* over a wide range in a single Co/Cu multilayer. Ion-irradiation monotonically decreases the GMR while subsequent annealing increases it. Compared with other techniques, this method has little effect on the crystallographic texture of the multilayer. Taken together, these results demonstrate that MeV ion bombardment can be a sensitive tool for interface modification in metallic multilayers and that, for Co/Cu multilayers, the GMR is indeed strongly dependent on the structure of the interface region.

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REFERENCES

1. M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Étienne, G. Creuzet, A. Friederich and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
2. M. Susuki and Y. Taga, Phys. Rev. **B52**, 361 (1995); J. Appl. Phys. **74**, 4661 (1993).
3. Eric E. Fullerton, David M. Kelly, J. Guimpel, Ivan K. Schuller, Phys. Rev. Lett. **68**, 859 (1992).
4. H. Zhang, R.W. Cochrane, Y. Huai, M. Mao, X. Bian and W.B. Muir, J. Appl. Phys. **75**, 6535 (1994); H. Lailer and B.J. Hickey, ibid **79**, 6250 (1996).
5. M. Cai, T. Veres, S. Roorda, R.W. Cochrane, R. Abdouche and M. Sutton, J. Appl. Phys. **81**, 5200 (1997).
6. D.M. Kelly, I.K. Schuller, K. Korenivski, K.V. Rao, K.K. Larsen, J. Bottinger, E.M. Gyorgy and R.B. van Dover, Phys. Rev. **B50** 3481 (1994); K. Temst, G. Verbanck, R. Schad, G. Gladyszewski and M. Hennion, Physica **B234-236**, 467 (1997).
7. Y. Huai, R.W. Cochrane and M. Sutton, Phys. Rev. **B48**, 2568 (1993).
8. J.F. Ziegler and J.P. Biersack, *The Stopping and Range of Ions in Solids*, Pergamon Press, New York, 1985.
9. P. Sigmund and A. Gras-Marti, Nucl. Instrum. Methods **182/183**, 25 (1993).
10. J. Kudrnovsky, V. Drchal, I. Turek, M. Sob, P. Weinberger, Phys. Rev. **B53**, 5125 (1996).