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Magnetoresistance Effect of Co–Cu Nanostructure Prepared by Electrodeposition Method

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It was possible to produce Co–Cu multilayer and alloy films controlled in the atomic scale by electrodeposition. We have examined the magnetoresistance (MR) in the Co–Cu multilayers and the alloy films produced by electrodeposition and have investigated the relationships between the magnetoresistance and film thickness, composition, and magnetization. For the Co–Cu multilayer films the maximum MR ratio at 300 K is about 16% (21 kOe) and at 5 K it increases to about 24%. The MR ratio is more strongly dependent on the Co alloy ferromagnetic layer thickness than the change of the composition near the interface between Co alloy and Cu layers. The giant magnetoresistance has also been observed for Co–Cu alloy films. The maximum MR ratio of the Co–Cu alloy films increases to 6.3% after annealing the film at 723 K for 1 hour. © 1999 Academic Press

Key Words: **giant magnetoresistance; multilayer film; Co–Cu alloy film; electrodeposition; magnetic properties.**

1. INTRODUCTION

The studies on the physical properties of metallic multilayers and alloy films prepared on the atomic scale have attracted attention in view of the fundamental physics and applications. Recent studies on giant magnetoresistance (GMR) in thin films are based on films grown mainly from the vapor phase. The phenomenon exhibits different properties depending on their production methods (1–4). However, the relationship between the production condition and the properties of the films is yet unclear. The GMR and the long-range exchange coupling between ferromagnetic layers due to the composition in the vicinity of the interface between ferromagnetic and nonmagnetic layers are unclear.

Electrodeposition is one of the advantageous methods for producing alloys and metallic multilayers of generally immiscible metal combinations (5–7). The electolytic metal growth differs from that of the vapor phase prinicipally due to the presence of the metal-solution double layer. Factors expected to cause differences are: (a) the existence of the electric field with strengths on the order of 10^7 Vcm^{-1} between electrode and ions in the double layer; (b) the charged nature of the particles arriving at the surface, etc. Therefore, it provides the possibility of depositing film structures different from those being produced from the vapor phase. The pulse electrodeposition method has a merit that it is possible to control the layer composition, the thickness of the multilayer, and the grain size by regulating the electrode potential wave (pulse amplitude), current density, and deposition time (pulse width), even from a single electrolyte (6–9).

We have examined the magnetoresistance (MR) in Co–Cu multilayers and alloy films produced by electrodeposition and the effect of the thickness and composition variation near the layer boundary between ferromagnetic and non-magnetic layers on the magnetoresistance and the relationships between the magnetoresistance and the magnetization. We have investigated how the properties of the films produced by electrodeposition are different from these of vapor deposition.

2. EXPERIMENTS

The electrolytic bath was composed of $CoSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, $Na_3C_6H_5O_7 \cdot 2H_2O$, and NaCl. The substrates for electrodeposition were copper thin films vapor deposited on glass plates. The Co–Cu multilayer films were grown using a simple square pulse and a trapezium-shaped pulse of 0.1–20 mA/cm^2. The Co–Cu alloy films were grown using a constant current density of 2 mA/cm^2 in plating solution maintained at a pH value of 6.0, and the thickness of the deposited films was 3000 Å. The composition of the deposited films was determined by X-ray fluorescence spectroscopy and atomic absorption spectroscopy. The MR ratio was calculated as $|\Delta R/R_0|$, where ΔR is the change in resistance due to the applied magnetic field and R_0 is the maximum resistance near zero magnetic field. The MR was measured at 300 and 5 K. The magnetic properties were investigated using a VSM, magnetic balance, and SQUID. The structure was analyzed by an X-ray diffractometer using Cu$K\alpha$ radiations.

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3. RESULTS AND DISCUSSION

3.1. Preparation of Films

Figure 1 shows the concentration of Co in the electrodeposited films as a function of the deposition current density. In the films deposited from a solution containing 93 at.% Co, the precipitation of Cu only is observed in the region of current densities less than 0.4 mA/cm^2 and the precipitation of the $Co_{86}Cu_{14}$ alloy is observed at and above 10 mA/cm^2. In the electrodeposition method, the current density does not only affect film composition, but also the grain size of the film (10). The composition of the ferromagnetic Co alloy layer has an effect on the thickness of the Cu layer showing the maximum MR ratio in the Cu layer thickness dependence of the MR ratio. Regulating either the deposition current density or the composition of the electrolyte solution, the composition in the ferromagnetic Co–Cu alloy layer can be changed. The Cu layer thickness dependence of the MR ratio shows the same tendency for the films deposited by changing deposition current density and the composition of electrolyte solution. And therefore, the experiments in regard to film composition change were carried out by two different methods, e.g., (a) changing the composition of electrolyte solution (at constant current density) in the region of 90–95 at.% Co and (b) changing the current density (0.4–20 mA/cm^2). It is possible to produce a multilayer film by using a constant periodic pulse electrode potential (say a and b in Fig. 1). If a trapezium shaped pulse, as shown with the broken line, is used instead of a simple square pulse then it is possible to modulate continuously the composition across the interface between the ferromagnetic Co alloy layer and the nonmagnetic Cu layer. By using a constant current density (say b or c in Fig. 1) an alloy film can be produced.

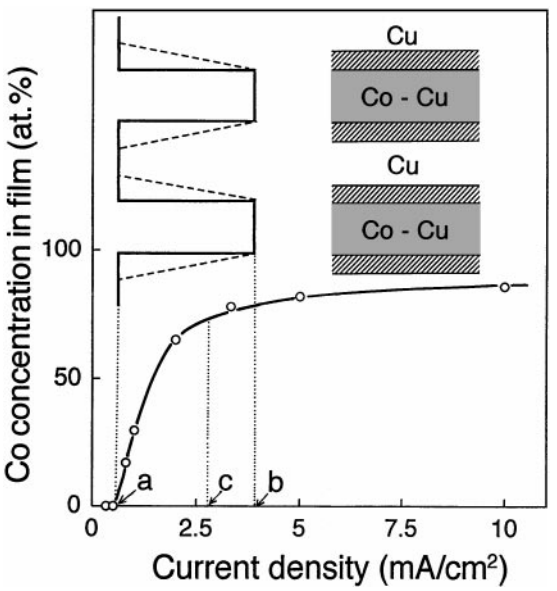

FIG. 1. Concentration of Co in electrodeposited films as a function of the deposition current density (bath composition is $Co_{93}Cu_7$), and the schematic diagram of the relation between the applied pulse wave shape (top left inset) and the deposited multilayer structure (top right inset). A simple square pulse (solid line in the top left inset) corresponds to a Co–Cu/Cu simple multilayer. A trapezium-shaped pulse (broken line in the top left inset) corresponds to a Co–Cu/Cu multilayer structure with a composition modulated layer between the ferromagnetic Co–Cu alloy layer and the nonmagnetic Cu layer (hatched line in the top right inset).

3.2. Magnetoresistance of Multilayer Films

Figure 2 shows the Cu layer thickness dependence of the MR ratio (at 21 kOe) measured at 300 and 5 K for the $[Co_{86}Cu_{14}$ 9 Å/Cu dÅ$]_{50}$ multilayers which were deposited with simple square pulse (current density of 0.33 and 20 mA/cm^2). Two peaks in the MR curves are observed at Cu layer thicknesses of 14 and 35 Å. The MR ratio has a maximum value of 16% at a Cu layer thickness of 14 Å (300 K, 21 kOe). The Cu layer thickness showing the maximum MR ratio is different from that of the sputtered deposited film. The reason seems to be that the composition of the ferromagnetic layer for the multilayer films produced by the pulse electrodeposition is not 100 at.% Co but contains Cu atoms. It is observed that the peak value of MR appears at a lower Cu layer thickness when increasing the Cu concentration in the ferromagnetic layer (6). Therefore, we assume that this Cu concentration in the ferromagnetic layer has an influence on the effective Cu nonmagnetic layer thickness. On annealing the films, the MR ratio of the films

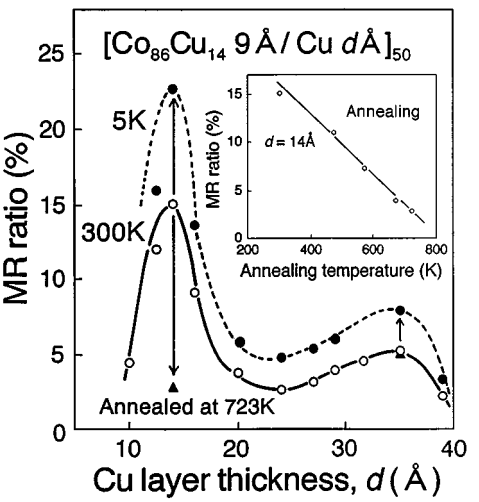

FIG. 2. Cu layer thickness dependence of the MR ratio (at 21 kOe) measured at 300 K for the $[Co_{86}Cu_{14}9$ Å/Cu d Å$]_{50}$ multilayer films deposited with a simple square pulse. The broken line is the MR ratio measured at 5 K. The inset shows the annealing temperature dependence of the MR ratio for the $[Co_{86}Cu_{14}9$ Å/Cu 14 Å$]_{50}$ multilayer film (annealed for 1 h).

with a Cu layer thickness of 14 Å decreases monotonically when increasing the annealing temperature and has a value of about 3% after annealing at 723 K for 1 h (inset of Fig. 2). The cause of the decrease of the MR ratio on annealing the film seems to be due to the phase separation in the ferromagnetic layer and/or diffusion of atoms across the interface in association with the change in interface flatness. When measured at a temperature of 5 K, the MR ratio increases for the all thicknesses of the Cu layer and has a maximum of 24% (Cu = 14 Å).

Figure 3 shows the magnetic field dependence of $\Delta R/R_0$ and the magnetization curve measured at 5 K for the $[Co_{86}Cu_{14}$ 9Å/Cu dÅ$]_{50}$ multilayer films (of Fig. 2) with different Cu layer thickness d. The $\Delta R/R_0$ value of the films with a higher Cu layer thickness d has a tendency to saturate relatively in a small magnetic field. In the field dependence of $\Delta R/R_0$, a double peak due to hysteresis is observed in the region of low magnetic fields. However, the magnetic field dependence of $\Delta R/R_0$ does not necessarily correspond precisely with the tendency of the magnetization curve in the wide field region. This disagreement seems to be due to the fact that the H_{peak} strongly depends on the magnetic properties in the ferromagnetic layer; that is, the change of the ferromagnetic layer structure arising from the increase in the nonmagnetic Cu layer thickness has an effect on the magnetism such as coercive force (e.g., H_{peak}). On the other hand, $\Delta R/R_0$ is closely related to the antiferromagnetic coupling of the magnetic layers adjacent to the nonmagnetic layers.

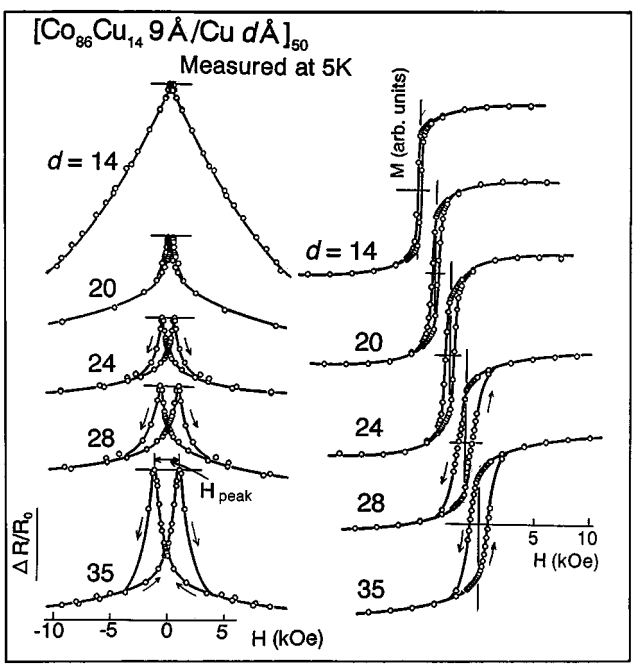

FIG. 3. Magnetic field dependence of the $\Delta R/R_0$ and magnetization curves measured at 5 K for the films of Fig. 2 with various Cu thicknesses.

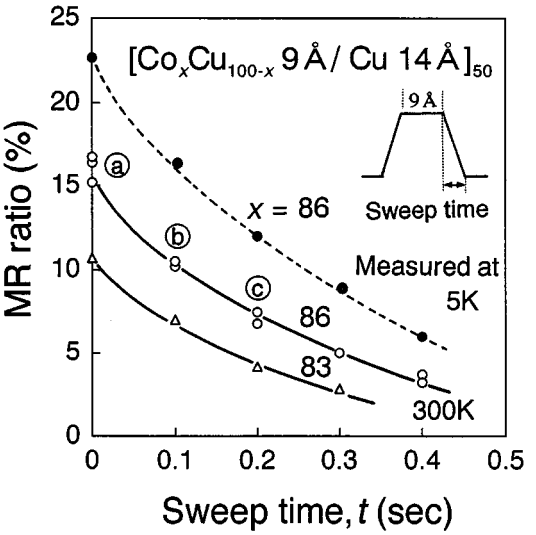

FIG. 4. MR ratio for the films with a ferromagnetic Co alloy layer thickness of 9 Å against the sweep time. The broken line is the MR ratio measured at 5 K for the films with a Co concentration of 86 at.% in the Co alloy layer. The inset shows the applied pulse wave shape.

By using a trapezium-shaped pulse we have tried to modulate gradually the composition across the interface between the ferromagnetic Co alloy layer and the nonmagnetic Cu layer. The multilayer film produced by a square pulse wave was that with Co alloy layer thickness of 9 Å and Cu layer thickness of 14 Å. In Fig. 4, we show the MR ratio of the prepared films against the sweep time to deposit the films. Here, the sweep time is proportional to the gradient of the trapezium-shaped pulse and corresponds to the thickness of the interface region. The MR ratio decreases monotonically with increasing sweep time. The MR ratios of the multilayer films with Co alloy layer composition of the 83 and 86 at.% Co show a similar tendency. When measured at a temperature of 5 K, the MR ratio considerably increases but has a tendency to decrease monotonically with increasing sweep time.

Figure 5 shows the sweep time dependence of the MR ratio for the films deposited using a trapezium-shaped pulse with a Co alloy layer thickness reduced to 4.5 Å. By increasing the sweep time, the MR ratio of these films first increases, exhibits a peak at sweep time of about 0.1 sec, and then decreases. A similar tendency was also observed for the films with different Co concentration (x = 83, 86, 88 at.%) in the ferromagnetic Co alloy layer. The intermediate layer thickness between Cu and the ferromagnetic Co alloy layer corresponding to a sweep time of 0.1 is estimated to be about 5 Å, by considering the increase of current efficiency with a decrease of the deposition current density. (For example, the current efficiency at 0.4 mA/cm^2 is about 85% and that at 20 mA/cm^2 is about 45%.) However, the composition in the intermediate layer changes over the range of

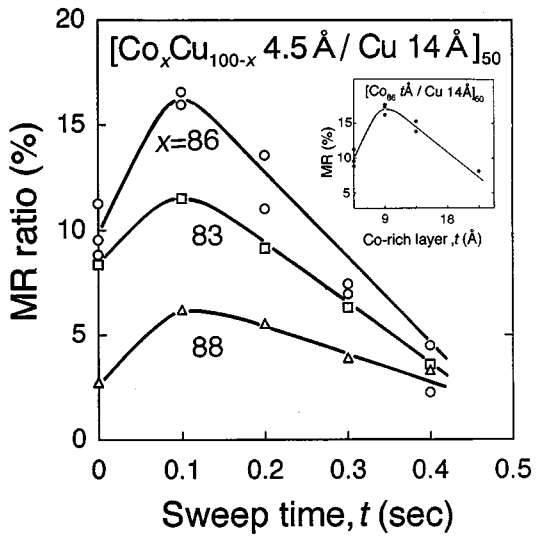

FIG. 5. MR ratio for the films with a Co alloy layer thickness of 4.5 Å and a composition of $x = 88$, 86, and 83 at.% Co against the sweep time. The inset shows the Co alloy layer thickness dependence of the MR ratio for the $[Co_{86}Cu_{14}t$ Å/Cu 14 Å$]_{50}$ multilayers deposited with a simple square pulse.

0–86 at.% Co. Therefore the thickness of the ferromagnetic layer is estimated as 4.5 Å by considering the fact that the electrodeposited Co–Cu alloys become ferromagnetic above 10 at.% Co in the alloys as shown in Fig. 9. The total thickness of the ferromagnetic layer therefore becomes about 9 Å. It seems from the results of Figs. 4 and 5 that an optimum Co alloy layer thickness of about 9 Å is necessary to have the highest magnetoresistance value. This can also be confirmed by the fact that the Co layer thickness dependence of the MR ratios of the films produced by square pulse shows a similar tendency as shown in the inset. A similar result has been reported by Parkin *et al.*, for sputter deposited film (11). Moreover, it seems to be that MR is more strongly dependent on the Co alloy layer thickness than the change of the composition near the interface between the Co alloy and the Cu layers. The difference in the experimental results of the sweep time dependence of the MR ratio, depending on the difference in the thickness (4.5 and 9 Å) of ferromagnetic Co alloy layers, suggests that comparatively flat film has been formed in atomic scale by electrodeposition.

Figure 6 shows the magnetic field dependence of $\Delta R/R_0$ and the magnetization curve for the films (a, b, c in Fig. 4). The magnetic field dependence of the film deposited without a sweep time (sweep time 0 sec) does not saturate in the region of the field; however, that of the film with a larger sweep time has a tendency to saturate in a relatively small magnetic field and also the MR ratio of the film decreases. The reason of the decrease in the MR ratio seems to be the following: With the increase of sweep time the Co alloy layer thickness increases; as a result the ferromagnetic coupling strengthens inside the Co alloy layer. Then the fraction of

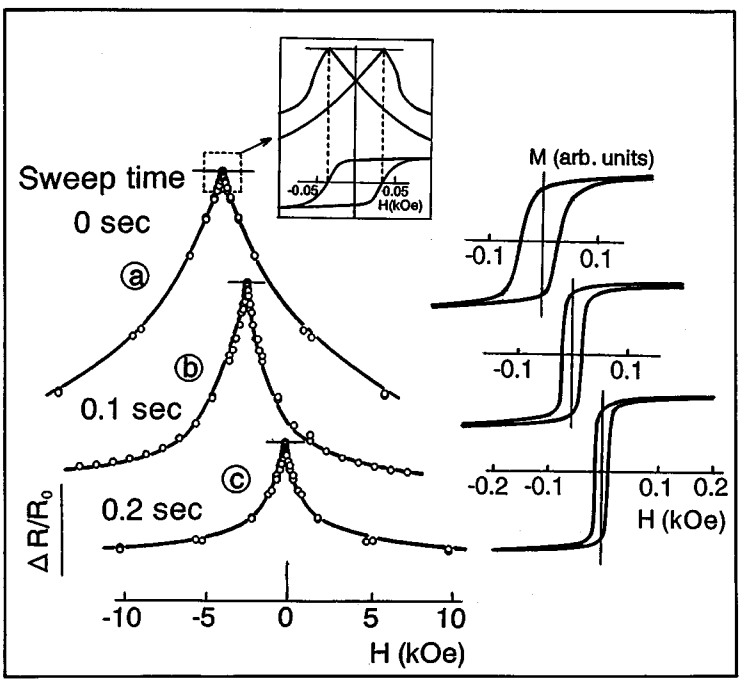

FIG. 6. Relationship between the magnetic field dependence of the $\Delta R/R_0$ and the magnetization curve for the $[Co_{86}Cu_{14}9$ Å/Cu 14 Å$]_{50}$ films deposited with sweep time of (a) 0, (b) 0.1, and (c) 0.2 sec. The inset shows the correspondence of the coercive forces (H_c) of magnetization curves to the peak of $\Delta R/R_0$ at low magnetic fields.

the region (volume fraction) in the ferromagnetic Co alloy layer which is still capable of remaining antiferromagnetically coupled to the adjacent ferromagnetic layer portion via the nonmagnetic layer decreases. In the low magnetic field, the H_{peak} in the field dependence of $\Delta R/R_0$ corresponds to the magnetic coercive force. The H_{peak} becomes narrow with the increase in the sweep time.

3.3. Magnetoresistance of Alloy Films

Figure 7 represents the X-ray diffraction patterns of the as-deposited Co_xCu_{100-x} films with Co concentration $x = 10$–54 at.%. The diffraction lines of fcc Cu single phases are only observed in the X-ray diffraction patterns, and the diffraction lines of (1 1 1) and (2 0 0) shift toward the higher angle side with an increase in the Co concentration. The shift of the diffraction line is attributed to the contraction of the Cu lattice due to the fact that Co atoms having an atomic radius less than that of Cu are dissolute in the atomic scale into the Cu matrix.

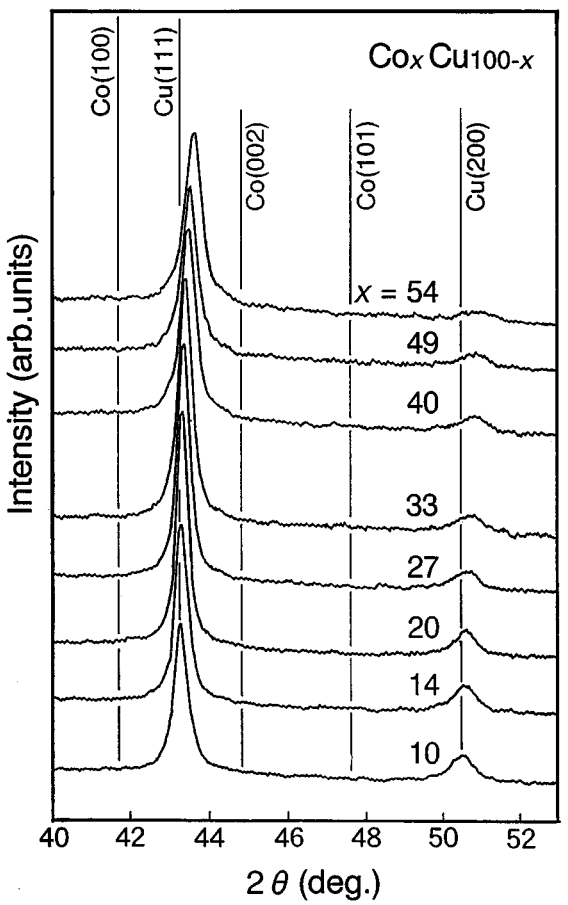

FIG. 7. X-ray diffraction patterns for the Co–Cu alloy films with various Co concentrations (X).

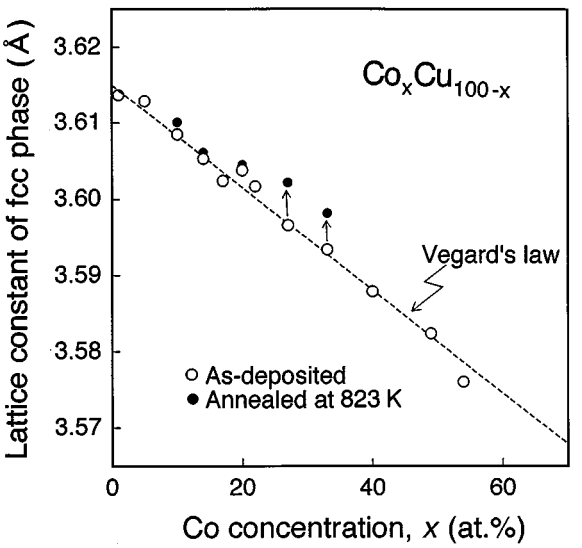

FIG. 8. Co concentration dependence of the lattice constants for the Co–Cu alloy films in the as-deposited and annealed state.

The lattice constants of the Co–Cu films estimated from the X-ray diffraction angle (Fig. 7) are plotted against the Co concentration of the film in Fig. 8. The lattice constants of the films decrease linearly with increasing Co concentration, and it follows Vegard's law. From the above result, it is considered that Co and Cu atoms are in a well-mixed condition; that is, to some considerable extent the Co–Cu alloy films form a solid solution. The lattice constant increases after annealing at 823 K.

Figure 9 shows the composition dependence of the saturation magnetization per weight of the Co–Cu alloy. The

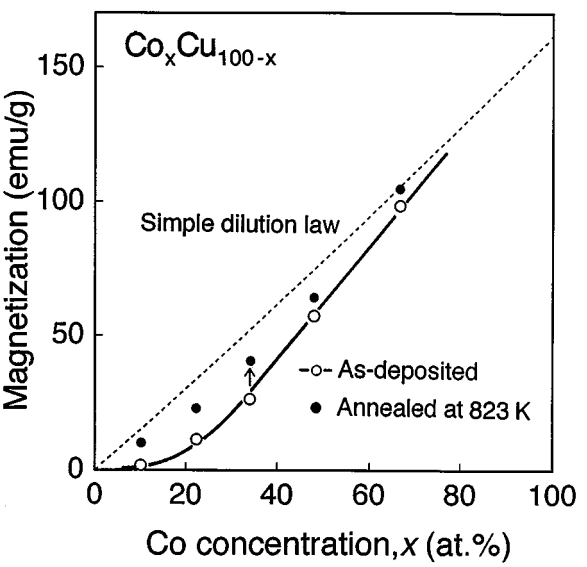

FIG. 9. Co concentration dependence of the saturation magnetization of the Co–Cu alloy films.

magnetization deviates downward from the simple dilution law, decreases monotonically with a decrease in the Co concentration, and vanishes at the Co concentration of 10%. This magnetization result also suggests that our Co–Cu alloys produced by electrodeposition formed a solid solution to a considerable extent. After annealing the films at 823 K for 1 h, the magnetization increases. The increase of magnetization and lattice constant (Fig. 8) can be attributed to the phase separation of the Co and Cu atoms.

Figure 10 shows the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization for the $Co_{27}Cu_{73}$ alloy films in the as-deposited state and after annealing at 723 K for 1 h. In the ZFC curve of the as-deposited sample a broad peak is observed near the temperature of 120 K. If the peak temperature is a blocking temperature observed for superparamagnetic behavior, the existence of the peak at the lower temperature side suggests that very fine particles of the ferromagnetic Co or Co–Cu alloy phase may have been precipitated in the deposition alloy film, and they have a wide distribution in their size. Existence of a (well-mixed) solid solution was inferred from the result of the composition dependence of the lattice constant (Fig. 8) estimated from X-ray diffraction and the result of the composition dependence of magnetization (Fig. 9) in Co–Cu alloy films. However, these exists the possibility of the presence of the small particles which cannot be detected by X-ray diffraction and/or cannot be concluded by the measurement of saturation magnetization. However,

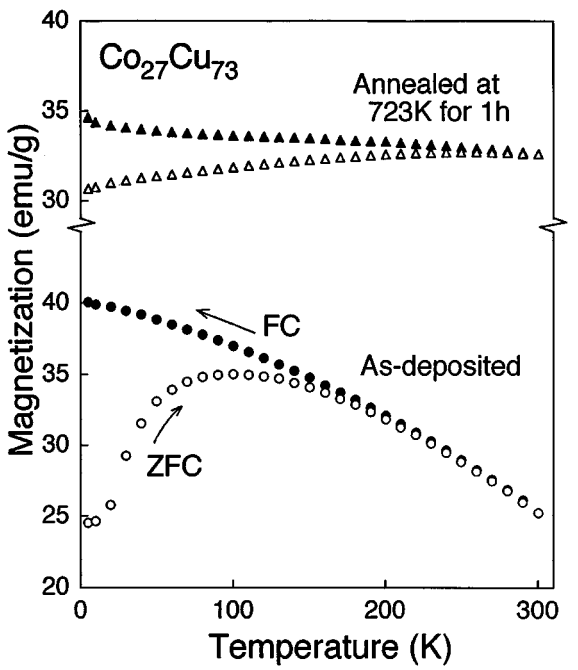

FIG. 10. Temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization for the $Co_{27}Cu_{73}$ alloy film in the as-deposited state and after annealing at 723 K for 1 h.

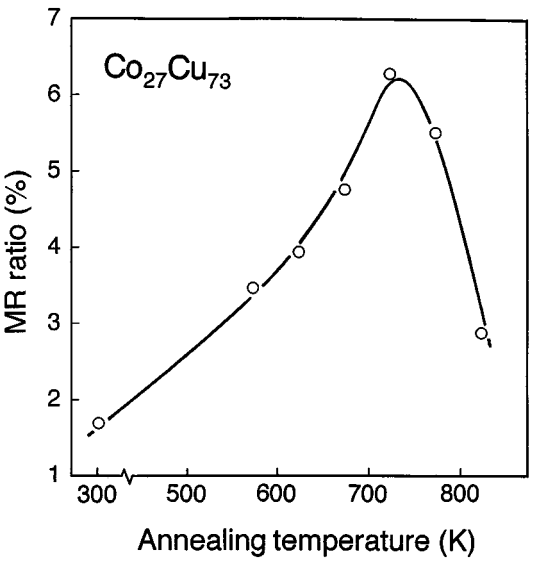

FIG. 11. Annealing temperature dependence of the MR ratio for the $Co_{27}Cu_{73}$ alloy film.

these precipitated ferromagnetic Co phases are not necessarily a Co single phase, but they may also be of a Co–Cu alloyed phase (solid solution). The MR ratio of about 1.8% has been observed for the $Co_{27}Cu_{73}$ as-deposited alloy films and after annealing at 723 K for 1 h the MR ratio increases to 6.3%. The presence of a 1.8% MR ratio in the as-deposited film is not contradictory with the possibility of the presence of ferromagnetic fine particles. On annealing at 723 K for 1 h, the ZFC curves show a ferromagnetic behavior. This indicates the existence of a large ferromagnetic particle having a blocking temperature above room temperature arising from the phase separation of Co and Cu.

The MR ratio of the $Co_{27}Cu_{73}$ alloy films against the annealing temperature is shown in Fig. 11. The as-deposited film,which seems to be in a solid solution state, has an MR ratio of only about 2%. Compared to that, the MR ratio of the film increases on annealing and exhibits a maximum value of 6.3% after annealing at 723 K. The reason for the increase in the MR ratio seems to be that phase separation of Co and Cu occurs due to annealing and the Co particle's precipitate in the film.

This temperature (723 K) corresponds to an optimum Co particle size at which the GMR becomes a maximum.

4. CONCLUSION

It was possible to produce Co–Cu multilayer and alloy films controlled in the atomic scale by electrodeposition.

Giant magnetoresistance has been observed in these films and the maximum MR ratio of multilayer films at 300 K is about 16% (21 kOe) and at 5 K it increases to about 24%. The MR ratio is more strongly dependent on the Co alloy

ferromagnetic layer thickness than the change of the composition near the interface between the Co ferromagnetic alloy and the Cu nonmagnetic layers. The optimum Co alloy layer thickness is about 9 Å.

The maximum MR ratio of the Co–Cu alloy films increases to 6.3% after annealing the film at 723 K for 1 h.

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