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Giant magnetoresistance in electro-deposited Co–Cu granular film

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Abstract. Co_xCu_{100-x} granular films have been successfully prepared by electrodeposition. The influences of deposition parameters and post-deposition annealing condition on giant magnetoresistance (GMR) have been studied in detail, using transmission electron microscopy (TEM), vibrating sample magnetometer and resistance measurements. It is found that, as for other methods, post-deposition annealing is crucial for obtaining larger GMR value. Under the optimum annealing condition, namely, annealing one hour at 695 K, GMR reaches a maximum value of -5% at room temperature, 1.3 T and -10% at 77 K, 0.9 T. A detailed TEM investigation shows that the grain size distribution follows a log-normal function. Using a recently developed model that takes explicitly into account the magnetic moment distribution (therefore grain size distribution) and spin-dependent electron–impurity scattering within magnetic grains and at the interface between grains and matrix for the granular films with superparamagnetic particles and considering the contribution from ferromagnetic grains, both experimental M–H and GMR–H curves have been well fitted with this log-normal size distribution. Our results confirm this model and evidence that the spin-dependent scattering at the interface between magnetic grains and non-magnetic matrix plays a dominant role for GMR, and grain size distribution is crucial in explaining the experiment results on GMR.

1. Introduction

The giant magnetoresistance (GMR) in multiplayer systems [1] and in granular films [2, 3] has stimulated a great deal of research activity due to both its fundamental scientific interest and its potential application for magnetic recording and magnetic sensors. Generally, granular films consist of two or more kinds of indissoluble metal in which small magnetic particles are embedded in non-magnetic metal medium. Theoretical studies [4] indicated that the GMR in granular films comes primarily from the spin-dependent scattering of conducting electrons both within ferromagnetic grains and at the interfaces between magnetic grains and non-magnetic matrix. Therefore, GMR is closely related to the features of magnetic granules such as the size, shape and distribution which, to a great extent, depend on the film making technology.

To date, Co–Cu granular films have been prepared by a variety of techniques including sputtering, electrodeposition (ED), splat cooling and mechanical alloying. Among them, electrodeposition is the simplest and cheapest one. It is a non-vacuum process, and structure is formed through electrochemical reaction in the solution. Therefore, from the point of view of both application and fundamental research, it is worth paying more attention to this technique. As well known, in most of the preparing methods as mentioned above, the occurrence and

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the value of GMR depend on the post-deposition annealing. In order to obtain optimum microstructure for maximum GMR, the choice of annealing condition is crucial, and it has been investigated extensively for the samples made by sputtering and splat cooling. However, less work concerns the annealing effect for electrodeposited films and some controversial statements still exist. For instance, some researchers concluded [5] that electrodeposited CuCo films are phase segregated immediately after deposition, i.e. they are not dependent on any subsequent annealing, while other researchers stated [6] that as-deposited Co–Cu films are in a solid-solution state, and upon annealing, Co and Cu phases separate, and consequently, the precipitation of Co fine particles occurs. Since the formation mechanism of electrodeposited films is different from those by other techniques, we need to investigate the microstructure evolution upon annealing and the relation to GMR, which is crucial not only in the application aspect, but also in the understanding of the underlying mechanism of GMR.

So far, many theories have been proposed to explain the magnetoresistance of granular films. Most studies consider the factors influencing GMR covering the size of granules, the average distance between granules, electronic mean free paths for each of the constituents, the ratio of bulk over interface scattering cross section and so on. Due to the complicated microstructure of these films, little work deals with the effect of the grain size distribution on GMR although it plays a crucial role in explaining the experiment results, as pointed out by many researchers [7]. Furthermore, more or fewer simplifications are introduced in explaining experimental results by using a theoretical model. For example, considering the grain size distribution always exists in real films, it is reasonable to suggest that in some cases, both ferromagnetic (FM) and superparamagnetic (SP) particles occur in these heterogeneous systems. M B Stearns' group [8] and S Honda *et al* [9] have taken into account the contributions of both FM and SP components on magnetization and GMR; however, they have not considered the grain size distribution. Recently, a complete study of the influence of magnetic moment distribution (i.e. grain size distribution) on GMR has been presented by E F Ferrari *et al* [10, 11]. However, as the first step of the study, they only considered the contribution of SP grains, and more direct experimental results on microstructure are needed to test this theoretical result. In this work, we have successfully prepared Co–Cu granular films by the electrodeposition technique and post-annealing. Co grain size distribution is obtained through experimental investigation by TEM and found to follow a log-normal function. Taking the advantages of the method given by M B Stearns *et al* in considering the contributions of both FM and SP components to magnetization and GMR and of that given by E F Ferrari *et al* in considering the size distribution of SP grains, we accomplished a direct comparison between the experimental results (e.g. magnetization, GMR and grain size distribution) and the current theoretical model in a more strict manner. Our study shows that both magnetization curve and GMR results can be fitted by considering a log-normal distribution of grain size; the latter is consistent with that obtained by direct TEM experimental investigation. Our results confirm the theoretical model of E F Ferrari and evidence that spin-dependent scattering in the interfaces between Co grain and Cu matrix plays a dominant role for GMR. To our best knowledge, this kind of research has not been reported.

2. Experiments

Co–Cu granular films were produced using a single electro-chemical cell and a three electrode system. Electrolyte contains: 39 g l^{-1} $CoSO_4 \cdot 7H_2O$, 4 g l^{-1} $CuSO_4 \cdot 5H_2O$, 86.6 g l^{-1} $Na_3C_6H_5O_7 \cdot 2H_2O$, 2 g l^{-1} NaCl and 16.2 g l^{-1} Na_2SO_4. A thin Cu layer ($\sim$3000 Å) is sputter deposited onto one side of a glass wafer as the working electrode. The electrodeposition was carried out with a current density about 1 mA cm^{-2} and deposited potential between -1.0 and

−1.2 V relative to the $Ag^+/AgCl$ reference electrode. The thickness of films was about 1.3 μm. TEM and energy dispersive x-ray analysis (EDX) methods were used to study the structure of films and identify the Co concentration, respectively. Magnetic properties were measured by vibrating sample magnetometer (VSM). The resistance and magnetoresistance were measured using the conventional four-terminal technique with magnetic field parallel to the film plane for the latter measurement. The GMR is defined as $\mathrm{MR} = \Delta R/R_0 = (R_0 - R_H)/R_0$, where R_H and R_0 refer to the resistance at applied magnetic field and zero magnetic field, respectively. The samples were annealed in a vacuum furnace with pressure of about 9.0×10^{-4} Pa.

Since underneath Co–Cu layer there is a layer of 3000 Å pure Cu which was deposited on a glass substrate as the working electrode, significant shorting of the current must occur in the Cu layer which will influence the measured GMR value. We treat this effect as follows.

Suppose the resistance of the Co–Cu granular film and pure Cu layer is R_m and R_c respectively, the measured resistance R_0 should be the total resistance of R_m and R_c in parallel, namely,

$$R_0 = \frac{R_c R_m}{R_c + R_m}. \tag{1}$$

Under a magnetic field, R_m changes to R_{mH} while R_c stays the same. Thus the total resistance becomes:

$$R_H = \frac{R_c R_{mH}}{R_c + R_{mH}}. \tag{2}$$

The measured magnetoresistance is:

$$\mathrm{MR}' = \frac{R_0 - R_H}{R_0} = \frac{R_c}{R_c + R_{mH}} \frac{R_m - R_{mH}}{R_m} \tag{3}$$

where $(R_m - R_{mH})/R_m = \mathrm{MR}$ is the real magnetoresistance of the sample.

Thus we have:

$$\mathrm{MR}' = \frac{R_c}{R_c + R_{mH}} \mathrm{MR}. \tag{4}$$

In the formula (4), the measured magnetoresistance MR′ depends on the relative value of R_c and R_{mH}: when $R_c \gg R_{mH}$, $\mathrm{MR}' \approx \mathrm{MR}$; $R_c \ll R_{mH}$, $\mathrm{MR}' \Rightarrow 0$; $R_c \approx R_{mH}$, $\mathrm{MR}' \approx \frac{1}{2}\mathrm{MR}$. This formula indicates that the shorting effect of the Cu layer decreases the measured magnetoresistance value. From formula (4), we obtain

$$\mathrm{MR} = \frac{R_c + R_{mH}}{R_c} \mathrm{MR}'. \tag{5}$$

So the real magnetoresistance can be obtained from this formula through R_c and R_{mH}. In our experiment, R_c is measured on a piece of pure Cu layer of 3000 Å with glass substrate which was taken from the pure Cu working electrode before depositing the Co–Cu film and has the same size and shape as those of the sample for GMR measurement. For the sample of $Co_{16}Cu_{84}$, R_c and R_{mH} are 0.340 and 0.119 Ω, respectively, while MR′ is 5.0% at RT under a magnetic field of 1.3 T, thus real MR = 7% which is much larger than the measured values. In this text, we still use the MR′ value instead of MR for simplicity.

3. Results and discussion

As shown in figure 1, Co concentration in the films increases monotonically with the movement of deposition potential toward the more negative side, indicating that the composition of films can be changed by controlling the potential. X-ray diffraction patterns of as-deposited films

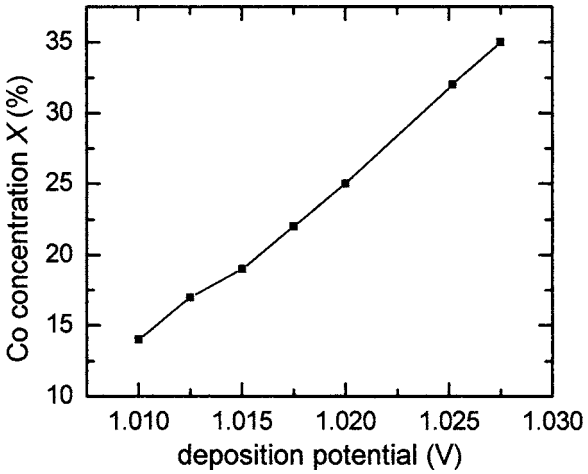

Figure 1. Deposition potential dependence on Co composition for Co_xCu_{100-x} films.

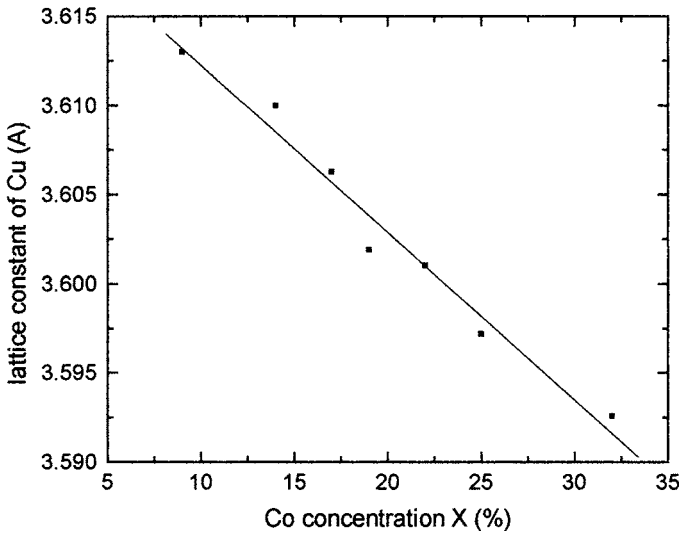

Figure 2. Relationship between lattice constant and Co composition for Co_xCu_{100-x} film.

show lattice constants intermediate between those of fcc Cu and fcc Co, and with the increase of Co concentration x, the lattice constants of the deposited films calculated from x-ray diffraction patterns decrease linearly (figure 2). This behaviour is similar to that of a Co–Cu solid solution. However, as will be seen later, in as-deposited samples, phase segregation occurs, but not completed, so both individual Co atoms and very fine Co particles or clusters are dispersed in the Cu matrix, which leads to the change of lattice constant with Co composition.

By annealing the $Co_{16}Cu_{84}$ specimen at various temperatures (T_a) for 30 minutes, the dependence of GMR and resistance on annealing temperature was obtained. As shown by figure 3(a), a peak appears at 695 K.

Figure 3(b) presents the variations of R_0 and ΔR with T_a in order to obtain a better understanding of the GMR–T_a curve. It is seen that R_0 decreases monotonically with T_a

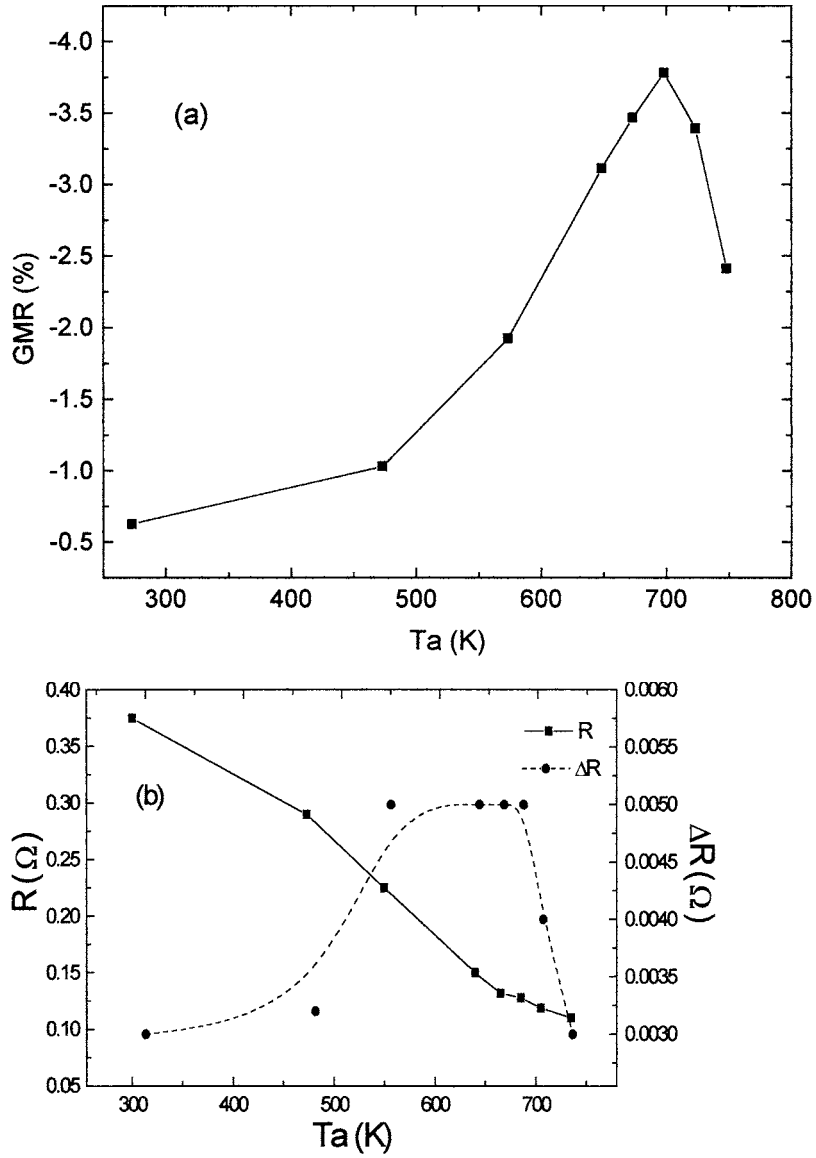

Figure 3. Dependence of GMR (a), resistance R and the deviation of ΔR (b) on annealing temperature T_a for $Co_{16}Cu_{84}$ sample.

increasing while ΔR exhibits an abrupt increase at $T_a = 473$ K, then keeps an almost unchanged value, and finally decreases at $T_a = 695$ K. This behaviour can be explained as follows: theoretical study [7] indicates that the magnetoresistance in granular films originates primarily from the spin-dependent scattering at the interface between granules and the matrix, and, to a lesser extent, from the spin-dependent scattering within the granules. Therefore, the ratio of the grain surface area to its volume (called the specific surface) is closely related to GMR. When the annealing temperature is low, the precipitation of Co phase from Cu matrix and the growth of Co grains occur slowly, but the annealing has relaxed the mismatch stress between

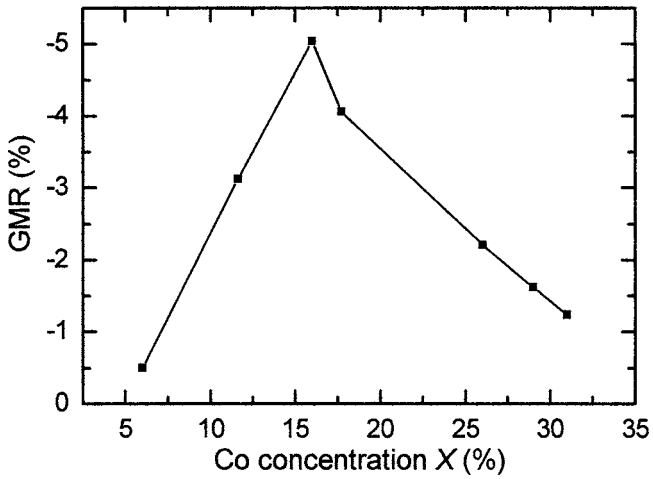

Figure 4. Composition dependence of GMR for Co_xCu_{100-x} films after one hour annealing at 695 K.

films and substrate, reduced defects and alleviated disorder, so the resistance of the films reduces, and as a result, the GMR gradually increases with increasing annealing temperature. When the annealing temperature becomes larger than 473 K, plenty of Co grains separate from the Cu matrix which increases the specific surface area of grains and therefore makes the GMR go up abruptly. With the further increase of temperature, the phase separation tends to stop, and ΔR tends to remain unchanged, but R_0 continuously decreases quickly due to the relaxation of stress and defects, which makes the MR continuously increase. When the increasing of temperature reaches some extant, for example, 695 K in our case, particles begin to grow, which decreases the specific surface of particles; at the same time, the decrease of R_0 becomes slower accompanying the completion of some relaxation of stress and defects. So GMR degrades. This structure evolution has been confirmed by TEM, as will be seen below.

At the optimum temperature determined from figure 3(a), a series of Co_xCu_{100-x} samples were annealed for one hour, then the relation between GMR and Co concentration was obtained, as shown in figure 4. The highest value of GMR appears at $x = 16$. Based on the above discussion, it is reasonable to suggest that when the composition of Co in the film is low, the number of magnetic grains is small; then the lack of scattering centres surely leads to the small value of GMR. With increasing Co concentration, the grains' number and size increase, so GMR tends to rise. As the further increase of Co composition, at a certain concentration to a certain extent, i.e. $x > 16$, GMR decreases. This behaviour can be explained as follows: with increasing Co concentration, a magnetic percolation threshold is reached so that neighbouring grains become strongly ferromagnetically coupled. Long before the actual Co percolation, a large ferromagnetic domain has formed: this makes the main contribution to the drop of GMR at large Co concentration.

Figure 5 shows the dependence of GMR on magnetic field H at RT and 77 K for the $Co_{16}Cu_{84}$ sample after an hour annealing. It is seen that GMR reaches -5% at room temperature, 1.3 T and -10% at 77 K, 0.9 T. The two GMR–H curves are far from saturated; therefore, the GMR values given here are underestimated considerably, but are still big enough for a relative comparison.

The structure evolution mentioned above has been confirmed by TEM. Figure 6 shows the bright-field, dark-field TEM images and the corresponding electronic diffraction patterns

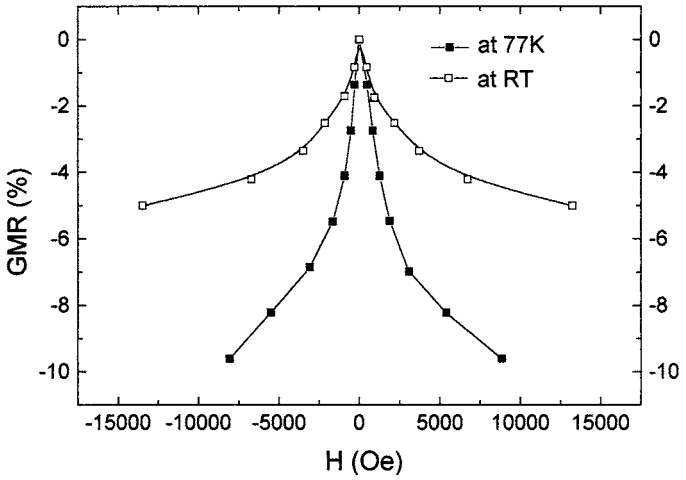

Figure 5. GMR versus magnetic field (H) at room temperature and 77 K for $Co_{16}Cu_{84}$ film after one hour annealing at 695 K.

of $Co_{16}Cu_{84}$ for states as deposited (a), (a′), (c) and after one hour annealing at 695 K (b), (b′), (c′), respectively. An increased average grain size after annealing has been clearly observed, and from the electronic diffraction patterns, these grains in Cu matrix are confirmed to have fcc Co structure. Based on the two images, we have presented statistics of the grain size as histograms shown in figure 7. Supposing the granular shape to be a sphere this histogram can be fitted with a log-normal distribution function

$$f(D) = \frac{1}{\sqrt{2\pi}\,DLn\sigma}\exp\left[-\frac{(LnD - Ln\bar{D})^2}{2(Ln\sigma)^2}\right] \tag{6}$$

where $\bar{D}$ is the average diameter of spherical granules, and σ is the normal deviation of the distribution. From this fitting, $\bar{D}$ and σ are obtained to be 10, 12 nm and 1.40, 1.60, before annealing and after annealing respectively. These curves help us to understand the change of GMR with the film microstructure more easily. It is seen that before annealing, the Co grain size mainly concentrates on a narrow range from a few to 20 nm with a maximum located at 9 nm. A number of theoretical studies have pointed out that the size of single-domain Co particles lies in the 11.4–32.0 nm range [12, 13], while the critical size of superparamagnetism for spherical particles at room temperature is 14.0 nm for fcc Co and 4.0 nm for hcp Co [14]. Thus, for our samples the Co particles before annealing are believed to have single-domain or superparamagnetic structures, and most particles are superparamagnetic. Therefore in a not high magnetic field, the GMR is small due to the difficulty of rotating the magnetization of superparamagnetic particles. After annealing, the grains grow, and new Co precipitation occurs, which makes the grain size distribution cover a wide range from a few to a few tens of nm, and in comparison with that before annealing, many more grains are in the range from 14 to 30 nm which is the range of single-domain Co particle size. In the same magnetic field, the magnetization of ferromagnetic particles is relatively easier to rotate than that of the superparamagnetic particles, which leads to the increase of GMR.

Magnetization study results support the microstructure and GMR behaviour mentioned above. Figure 8 presents the M–H curves in as-deposited (a) and after one hour annealing at 695 K (b) states for the $Co_{16}Cu_{84}$ sample. It is immediately found that the annealed sample has a larger H_c than the as-deposited one, which can be attributed to the existence of more

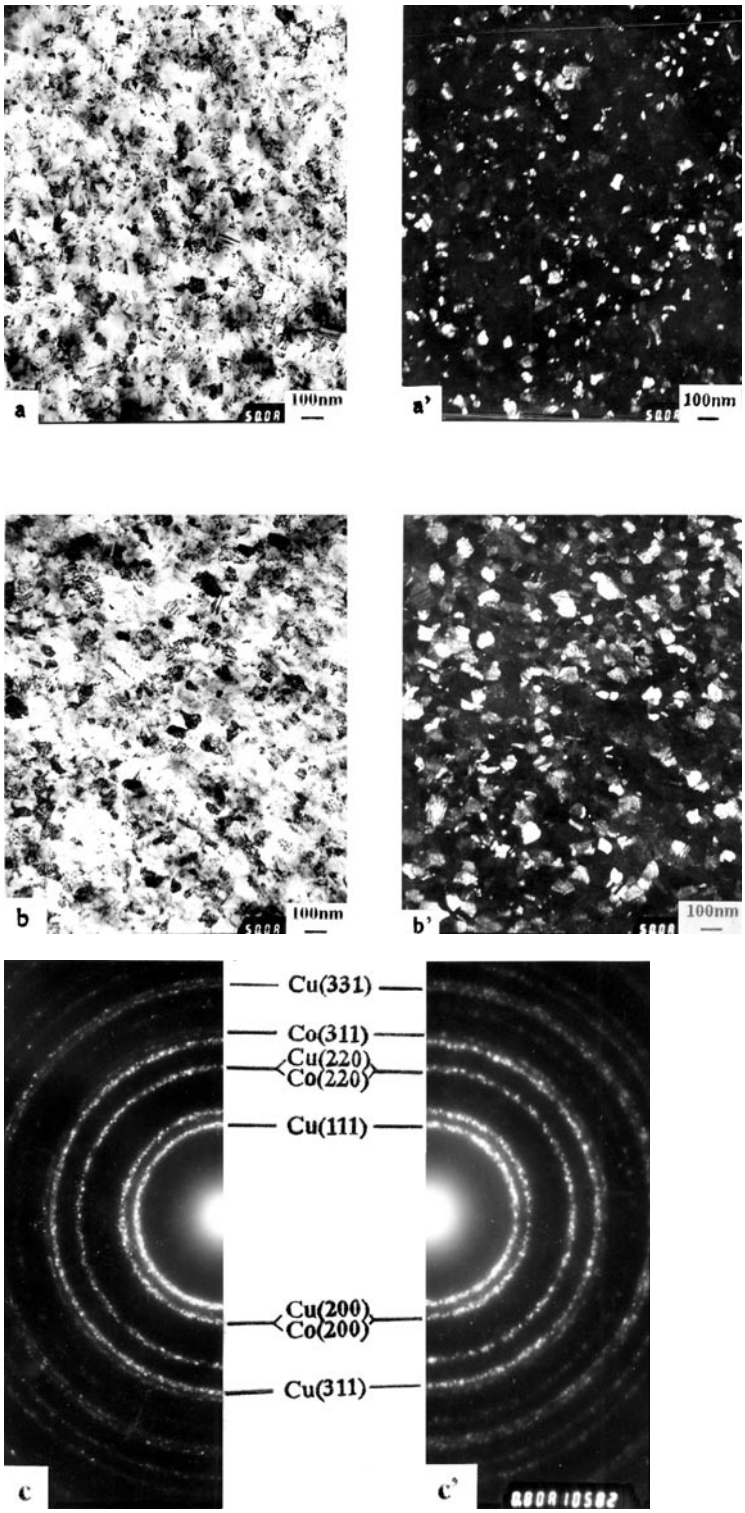

Figure 6. Bright-field TEM image (a), dark-field TEM image (a′) and electronic diffraction patterns (c) of $Co_{16}Cu_{84}$ film for as-deposited, and (b), (b′), (c′) for one hour annealing at 695 K states.

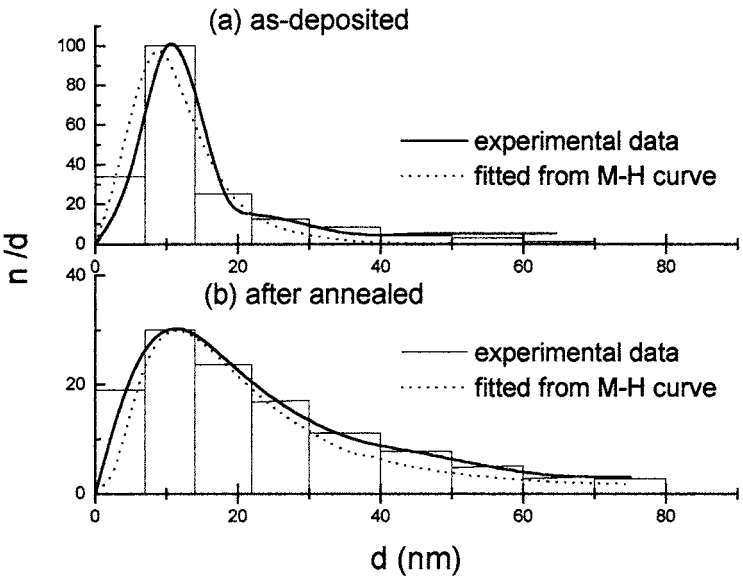

Figure 7. Grain size distribution (solid lines) of $Co_{16}Cu_{84}$ in as-deposited (a) and annealed (one hour at 695 K) (b) states from TEM, and the fitted results (dotted lines) from formula (8).

single-domain particles in annealed samples. According to the above discussion on TEM, the grain size covers a wide range and follows a log-normal distribution. So it is reasonable to consider that the system contains both ferromagnetic and superparamagnetic particles, and both of them contribute to M and GMR. S Honda *et al* [9] adopted the following expression to fit the contributions of two parts for the experimental curves:

$$M(H) = \frac{2M_{FM}^2}{\pi}\tan^{-1}\left\{\frac{H \pm H_c}{H_c}\tan\left(\frac{\pi M_{FM}^r}{2M_{FM}^s}\right)\right\} + M_{SP}^s\left\{\coth\left(\frac{\mu H}{k_B T}\right) - \left(\frac{\mu H}{k_B T}\right)^{-1}\right\} \quad (7)$$

where M_{FM}^s, M_{FM}^r and H_c are the saturation magnetization, remanence and coercivity of the ferromagnetic component, and M_{SP}^s and μ are the saturation magnetization of the superparamagnetic part and average magnetic moment of a superparamagnetic particle, respectively. In our formula, the particle size distribution has not been taken into account. In this work, considering the particle size distribution $f(D)$ given by formula (6), the formula (7) becomes

$$M(H) = \frac{2M_{FM}^s}{\pi}\tan^{-1}\left\{\frac{H \pm H_c}{H_c}\tan\left(\frac{\pi M_{FM}^r}{2M_{FM}^s}\right)\right\} + M_{SP}^s\int_0^\infty L(V)f(V)\,\mathrm{d}V \quad (8)$$

where L is the Langevin function, V is the particle volume. The fitting curves are shown in figure 8. It can be seen that the fitting curve (line) is consistent with the experimental curve (dots) quite well. The fitted parameters are $\bar{D}' = 9.0$, 13.0 nm, $\sigma' = 1.41$, 1.59 for as-deposited and annealed samples, respectively.

Equally, considering the particle size distribution and the ratio between the interface and bulk scattering cross sections, we obtained the magnetoresistance in the following form

$$\mathrm{MR} = -A\left[\left(\frac{M_{FM}(H)}{M_{FM}^s}\right)^2 - \left(\frac{M_{FM}^r}{M_{FM}^s}\right)^2\right] - B\left[\int_0^\infty (1+\alpha V^{1/3})L(V)f(V)\,\mathrm{d}V\right]^2 \quad (9)$$

where $M_{FM}(H)$ is the magnetization at magnetic field H. The second term comes from the formula (2) of [10], where A and B are proportional coefficients, and α is a parameter

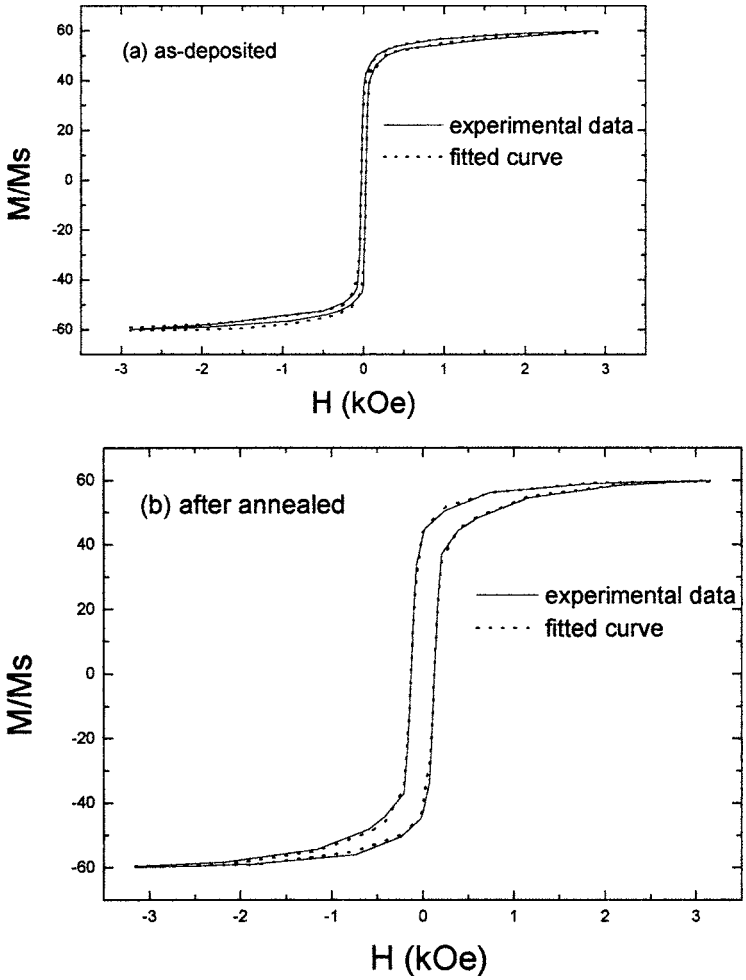

Figure 8. Experimental (solid lines) and fitting (dotted lines) M–H curves of $Co_{16}Cu_{84}$ film in as-deposited (a) and annealed (one hour at 695 K) states (b).

directly related to the ratio between the interface and bulk scattering cross sections. Using the distribution function given by equation (6) with exactly the same parameters obtained from the fitting of the M–H curve, we performed the fitting for the GMR–H curve of the $Co_{16}Cu_{84}$ sample with equation (9). In this case, only the parameter, α, was adjusted. Figure 9 shows the fitted curve in comparison with that from experiment. The two broken lines come from the first and second terms of equation (9), respectively. The resultant curve (solid line) agrees well with the experimental curve (dotted curve), indicating a good coincidence between theory and experiments. From the fitting data, we obtained $\alpha = 28.7$, implying the electron scattering from interface between Co particles and Cu matrix dominates the GMR. This figure also shows that in lower field the FM curve fits the GMR–H curve better, which means that the larger particles have a bigger contribution to GMR in this range, and the fitting of the SP curve indicates that the tiny particles have a bigger contribution in very high magnetic field.

The size distribution function $f'(D)$ used in fitting M–H and GMR–H curves is also shown in figure 7 by dotted-line curves for as-deposited and annealed samples. In comparison

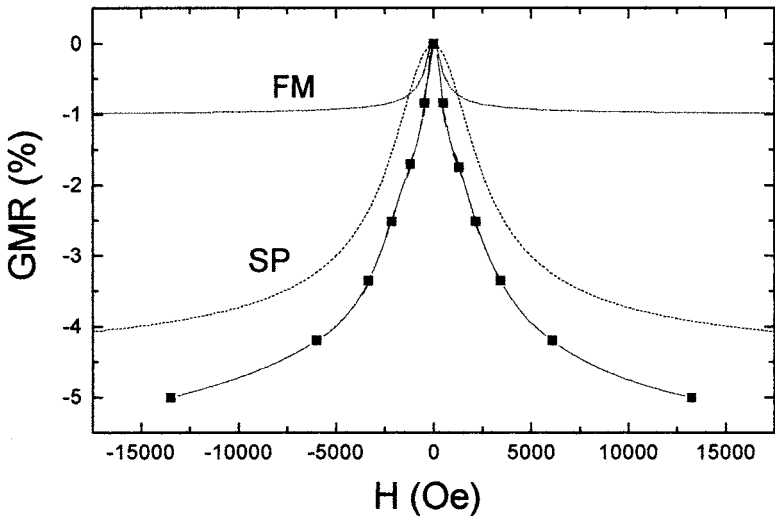

Figure 9. Experimental (dots) and fitting (solid lines) GMR–H curves for the $Co_{16}Cu_{84}$ film after one hour annealing at 695 K.

with the experimental curves $f(D)$ by TEM (solid line), we found a small discrepancy between $f'(D)$ and $f(D)$ curves which is caused by the error in counting the particle size distribution. Nevertheless, the fitted parameters, $\bar{D} = 9.0$, 13.0 nm; $\sigma' = 1.41$, 1.59 for $f'(D)$ and $\bar{D} = 10$, 12 nm; $\sigma = 1.40$, 1.60 for $f(D)$, have no big difference, indicating the agreement of the theoretical model by Ferrari with the experimental results. Since the applied maximum magnetic field in this work is only 1.3 T, we only tested the model in this field range.

4. Conclusions

We have successfully fabricated Co–Cu granular films by electrodeposition and studied their structure, electrical and magnetic properties. We found:

(1) As-electrodeposited film is phase segregated but not completely. Therefore post-deposited annealing is crucial for obtaining maximum GMR by controlling the microstructure of the films. Optimum conditions, namely, annealing for one hour at 695 K, a GMR of -5% at room temperature under 1.3 T and -10% at 77 K under 0.9 T are obtained for the sample with optimum Co concentration, i.e. $Co_{16}Cu_{84}$.

(2) The granule size distribution plays a very important role in GMR. TEM investigation shows a log-normal distribution for grain size. The experimental M–H curves have been well fitted by a model which considers the contribution from both ferromagnetic and superparamagnetic grains with this distribution. At room temperature, in not high magnetic field, single-domain ferromagnetic grains give a large contribution to GMR, while in very high magnetic field, superparamagnetic grains makes the main contribution to GMR.

(3) The validity of the theoretical model of Ferrari has been confirmed in dealing with the GMR in granular films with grain size distribution for the field below 1.3 T. The results on the present Co–Cu granular films evidence again that the spin-dependent scattering in the interface between grain and matrix dominates the GMR.

Acknowledgment

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