Annealing effect on the structural, magnetic and transport properties in the Co_xCu_{1-x} granular alloys with $0.20 \le x \le 0.25$ prepared by the ion-beam sputtering technique

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We have studied the transport and magnetic properties of a metallic granular $Co_x Cu_{1-x}$ system, with $0.2 \le x \le 0.25$, prepared by using a ion-beam sputtering technique. Giant magnetoresistance (GMR) has been observed for the all studied concentration with the average amplitude around 2%. at 300K. The maximum value has been observed for $Co_{21}Cu_{79}$ granular alloy after annealing at 450°C for 2h. Above this concentration the MR decreases which is attributed to the percolation effect, which causes a concurrent reduction in magnetic coercivity. The variation of magnetic and transport properties with the concentration and annealing time is discussed.

I. Introduction

Granular films are magnetic composite materials that usually consist of nanoscale magnetic granules embedded in an immiscible metallic matrix, or in an insulator [1,2]. Those systems, which include Cu-Co[3-5], Cu-Fe[4], Co-Ag[6.7], Fe-Ni-Ag[8.9], and Fe-Co-Ag[10] alloys, exhibit giant magnetoresistance (GMR) effect[3.4], and have interesting potential application in microelectronic devices.

Several techniques, such as evaporation, sputtering, mechanical alloying, and melt spinning, can be used to produce immiscible granular alloys; subsequent heat treatment of the sample allows the formation of nanoscale magnetic granules. The studies of granular materials to date have been focused on systems in which the granules are elemental metals[1-4], while granular metals in an insulating medium have been explored for quite some time, those in a metallic medium are more recent ventures [11.12].

The GMR effect in granular metals, as well as in metallic multilayers, is well known to be related to the spin-dependent scattering of the conduction electrons and to the reorientation of the magnetic moments by an external magnetic field[13.14]. In a zero applied field, the magnetic moments of the granules are supposed to be oriented randomly in space, and the resistance, in both the spin-up and spin-down channels, is considerably high. The alignment of the moments, however, leads to a short-circuit effect in one of the spin channels, with a consequent decrease of the total resistance of the system. It is shown that the amplitude of the MR depends strongly on the size of the magnetic granules and on the fabrication procedure. Therefore, appropriate annealing procedure is an important requirement for obtaining high performance materials.

In this work, we have used a number of experimental techniques including X-ray diffraction, alternating-gradient force magnetometer (AGFM) and four-terminal magnetoresistivity geometry to characterise the ion beam sputtered $Co_{1-x}Cu_x$ granular alloys. This allows the investigation of the Co phase separation process, magnetic and transport properties and their relation with the composition and annealing conditions. The variation of these properties with the concentration and annealing time is reported and discussed.

II. Experimental details

Co-Cu thin film samples were prepared using the ion-beam sputtering (IBS) technique. The high vacuum system is equipped with a kauffman ion gun. The base pressure was 1×10^{-8} mbar and sputtering was carried out using 2×10^{-4} mbar argon ions. After being ionised in the high voltage chamber, the argon ion beam bombards the target at the incidence angle of 45°. The beam voltage was 400 V and the beam current around 1mA. The growth rates were typically around 0.7 nm/min and 1.6 nm/min for Co and Cu layers respectively. The samples are deposited at room temperature on a glass substrate covered by a 5 nm Fe layer. A series of samples with different Co concentration were fabricated. The film thickness was fixed around 1000Å.

III. Results and discussion

The X-ray measurements were performed at room temperature using a Siemens powder diffractometer with monochromatic Cu or Co $K\alpha_1$ radiation. The geometry of the diffractometer allows only experiments in reflection mode. X-ray spectra of the as sputtered Co_xCu_{1-x} samples are reported in figure 1, and are characteristics of single-phase metastable alloys. The structure of this single-phase is fcc, and the diffraction peaks observed in these spectra for the whole composition are almost identical, with except the

progressive shift toward high angles observed for the Cu diffraction peaks with increasing the Co content in the film. Two diffraction peaks are clearly distinguished at 2θ = 43.2° and 2θ = 50.2°, which correspond to the (111) Cu and (200) Cu planes respectively. The lattice parameters of the Cu matrix calculated using the 2θ angle of the diffraction peaks is intermediate between those of bulk Co and bulk Cu[11].

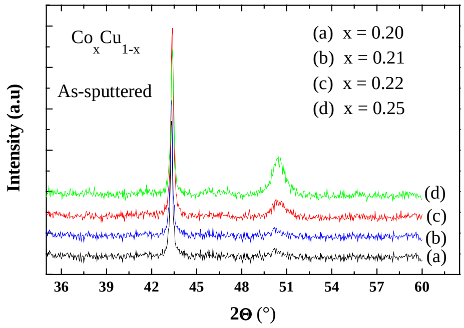

Figure 1 : High angles X-ray diffraction spectrum taken at 300 K with Cu $K_{\alpha 1}$ radiation for the as-deposited Co_xCu_{1-x} granular samples.

In the as sputtered state, the lattice parameters of Cu matrix decreases with increasing Co concentration due to smaller Co atoms dissolved in Cu matrix beyond the equilibrate limit leading to the lattice shrinkage. This effect is further confirmed in the figure 2, which shows the variation of the spacing of (111) planes, d_{111}, as a function the Co concentration. Such a systematic decrease in the d_{111} with increasing the Co concentration is consistent with a metastable solid solution.

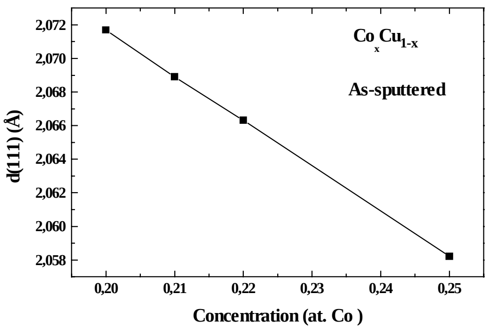

Figure 2 : d_{111} spacing of the (111) Cu planes as a function of the Co concentration for the as-deposited Co_xCu_{1-x} samples.

The magnetic properties of the Co_xCu_{1-x} samples have been studied using an alternating gradient force magnetometer (AGFM) with the magnetic field applied in the plane of the films. Figure 3 shows typical hysteresis loops obtained at room temperature on the as-sputtered samples for various Co concentrations. Very small hysteresis and small remanent magnetisation are observed in these systems for the whole concentration. The saturation of the magnetiszation has not been achieved even in magnetic field as large as 15 kOe.

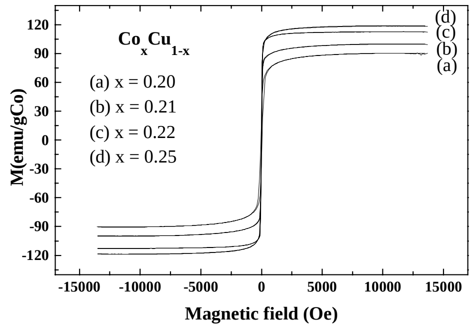

Figure. 3 : Hysteresis loops at 300K for the as-deposited Co_xCu_{1-x} granular samples.

This is not clearly distinguishable due the slow slope approach to the saturation and will be confirmed later using MR measurements. Not withstanding, we will use in the next part the term saturation magnetization, which means the magnetization at 15 kOe, in order to make the understanding easier for the reader. Figure 4 shows the variation of the saturation magnetization, M_S per gram of Co, with the Co concentration for the as-sputtered and annealed Co_xCu_{1-x} samples at 450°C during 30 min. As already shown in figure 3, in the as-sputtered state, M_S increases significantly with increasing Co content to reach the value of 122 e.m.u. /g of Co for 22 % at Co. This value is smaller than the bulk Co value 164 e.m.u./g[11]. This means that an important amount of Co particles has not precipitate in the as-sputtered state. Therefore, after annealing the as-deposited samples at 450°C during 30 min, a strong increase in the magnetization saturation has been observed, to reach an average value of 142 e.m.u./g for the whole concentration.

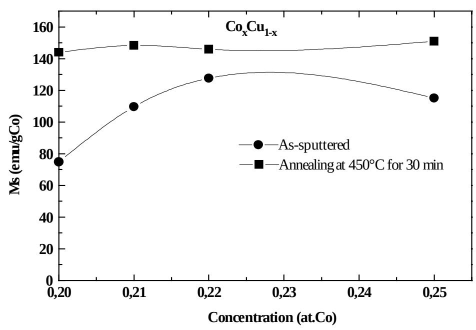

Figure 4: Saturation magnetization Ms,per gram of Co, versus of the Co concentration for the as-deposited Co_xCu_{1-x} samples (full circles) and annealed Co_xCu_{1-x} samples at 450°C for 30 min (full squares).

This value is still below the bulk value even after

annealing at 450°C for 2h, and indicates that the Co phase precipitation occurred during annealing process is not perfect. As a consequence, the magnetic phase separation is incomplete, and some Co atoms are still dissolved in the Cu matrix.

In order to have more information on the phase separation, magnetoresistance measurements as function of the magnetic field have been performed at room temperature for the as-deposited and annealed sample. Figure 5 shows the MR results for the as-sputtered Co_xCu_{1-x} granular alloys. All the MR curves are similar presenting a triangular variation of the resistance against the magnetic field and no saturation for applied magnetic field as large as 17 kOe, which are typical characteristics of granular alloys.

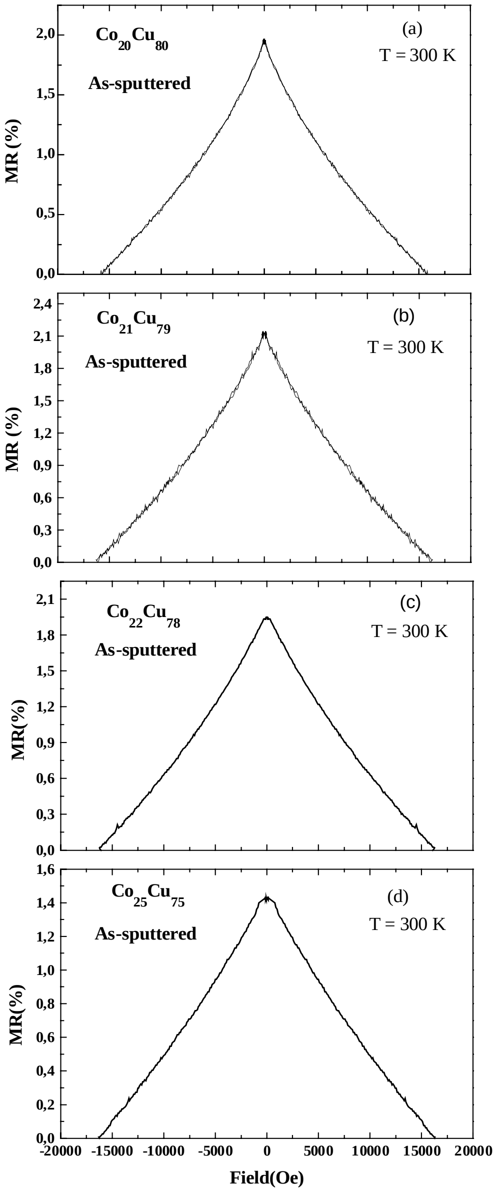

Figure 5 : Magnetoresistance curves at 300 K for Co_xCu_{1-x} alloys: (a) ($Co_{20}Cu_{80}$); (b) ($Co_{21}Cu_{79}$); (c) ($Co_{22}Cu_{78}$); and (d) ($Co_{25}Cu_{75}$). The magnetic field is applied in the film plane parallel to the current direction.

The MR values are small in the as-deposited state and increase with the Co concentration to reach a maximum of 2.25% for 21 % at Co, and decreases above this concentration to 1.5% for 25 % at Co (figure 6). This drop is mainly due to the increasing coalescence of the magnetic particles, as the Co concentration increases, and it is more likely for the magnetic particles to connect to adjacent ones to form clusters networks. Therefore, the interaction among neighbouring Co particles becomes more important. In addition, the reduction of effective surface area of the formed large clusters is also a source of the reduced GMR effect, since the magnetic surface scattering plays a dominant role. The observation of a relatively low MR for the as-sputtered samples is attributed to the formation of small Co particles during the deposition. As the Co concentration increases, the magnetic clusters become larger in size, and consequently the MR is reduced due to the appearance of coupling between neighbouring Co clusters, and the system becomes closer to the magnetic percolation.

Figure 6 presents the MR ratios measured at room temperature for the Co_xCu_{1-x} alloys as a function of the Co concentration. The evolution of the MR of the as-sputtered alloys has been already discussed in the last paragraph. The same evolution has been obtained for the annealed alloys at 450°C for 30 min. Indeed, in the magnetically dilute region, the MR increases with the concentration, due to the increase of the magnetic scattering centres, to reach 3% for x = 0.21. Above this concentration, the MR decreases to reach 1.7% for x = 0.25 for the same reasons as developed above.

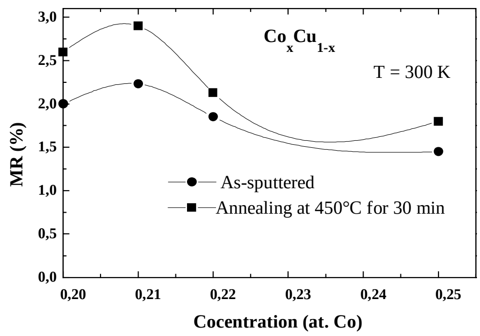

Figure 6 : Variation of the magnetoresistance as function of the Co concentration for as-deposited Co_xCu_{1-x} samples (full circles) and annealed Co_xCu_{1-x} samples at 450°C for 30 min (full squares).

All the reported results show that the optimum magnetotransport characteristics are obtained for x = 0.21. For this reason we focus our discussion in the next part on the $Co_{21}Cu_{79}$ alloy.

In figure 7 we report the magnetoresistance curves measured at room temperature for the as-sputtered and annealed $Co_{21}Cu_{79}$ alloy at 450°C with different annealing time. Already for

annealing during 30 min, the MR increases with respect to the value obtained for the as-sputtered alloy. As the annealing time increases, the MR increases. This dependence of the MR on the annealing time is related to the change in the microstructure of the sample, mainly the size of the Co particles and their distribution in the Cu matrix. The maximum of the magnetoresistance variation reaches 16% after annealing for 2h[15]. At this temperature, we can probably assume that the sample has a higher magnetic particles surface-to-volume ratio that acts as the conduction electron spin-dependent scattering centres[16,17,18]. The MR remains unsaturated even at 17 kOe probably due to the slow approach to the saturation of the small particles[19,20].

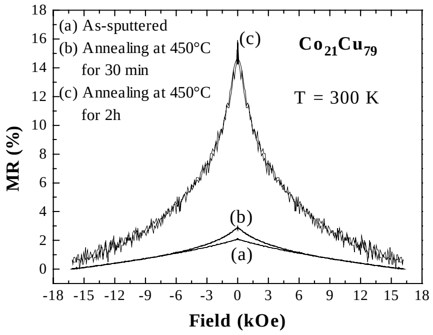

Figure 7: Magnetoresistance curves at 300 K for $Co_{21}Cu_{79}$ granular film : as-deposited (a) and after annealing at 450°C for 30 min (b) and 2 hours (c).

It is now widely accepted that magnetoresistance in the granular systems is a resistance due to spin-dependent scattering from non-aligned ferromagnetic particles. Therefore, a correlation between MR and magnetization is obvious. Xiao et al.[4] suggested that the magnetoresistance in the granular systems can be expressed as

$$\Delta R/R = -F(M/Ms),$$

where M is global magnetization and M_S the saturation magnetization. An important factor for the GMR in the granular systems is the average $<\cos\theta_{ij}>$, where θ_{ij} is the angle between the axes of the particles magnetic moment. If these particles are assumed not magnetically correlated, we find[21] that $<\cos\theta_{ij}> = <\cos\theta_i>^2 = (M/Ms)^2$, where θ_i is the angle between the moment of the i-th particle and the magnetic field direction. Thus, the function F(M/Ms) is proportional to $(M/Ms)^2$, and consequently $\Delta R/R = -A(M/Ms)^2$, where A determines the amplitude of the GMR. This parabolic behaviour has been previously reported[4]. In order to see if such function also applies in our case, we have reported in figure 8 the MR curves as function of the normalised magnetisation, M/M_S, for three $Co_{21}Cu_{79}$ alloys: as-sputtered, and the annealed at 450°C during 30 min and 2 hours, respectively. The parabolic behaviour predicted by the independent-moment model is not obtained in the present situation. Indeed, the deviation from such behaviour and particularly in the low M/Ms region is, however, not unusual, and often mentioned as a proof of the existence of magnetic interactions among the magnetic particles. This is in agreement with the magnetization curves showing a non-negligible remanent magnetization. Moreover, the remanent magnetisation is strongly enhanced after annealing at 450°C during 2 hours, which explains the fact that the deviation from the parabolic behaviour is more pronounced in this case as shown in figure 8c.

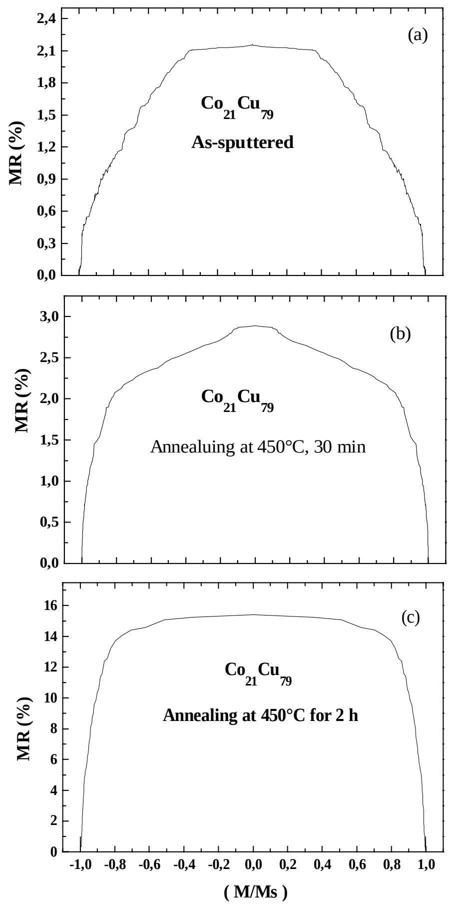

Figure 8: Magnetoresistance curves as function of normalised magnetization, M/M_S, at 300 K for the $Co_{21}Cu_{79}$ granular sample : as-deposited (a) and after annealing at 450°C for 30 min (b) and 2 hours (c).

IV. Conclusion

We have investigated the magnetic properties, and the GMR of Co_xCu_{1-x} granular alloys with $0.20 \le x \le 0.25$ in the as-sputtered and annealed states. The variation of GMR with Co composition has been shown There is a maximum of GMR at x = 0.21, near the percolation threshold. The decrease of GMR at high concentration is attributed to the increasing coalescence of the magnetic particles.

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