Giant magnetoresistance and its dependence on processing conditions in magnetic granular alloys

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We have studied giant magnetoresistance (GMR) effect and its dependence on processing conditions in Fe-Ag and Co-Ag alloys made by magnetron sputtering. The effect of elevated substrate temperature on GMR has been investigated and compared with the results of post-deposition annealing. As a unique feature, *in situ* annealing yields a second GMR peak at high deposition temperatures, which is associated with a substantially reduced saturation field for GMR. Deposition rate was found to be another crucial parameter in affecting GMR, whereas little effect was observed in varying the sputtering gas pressure.

Since its discovery in magnetic multilayers[1–3] and granular materials,[4,5] the giant magnetoresistance (GMR) effect has been found to depend sensitively on material parameters and processing conditions. Studying the correlation between GMR and processing conditions is crucial not only in the application aspect, but also in the understanding of the underlying mechanism of GMR. It has been commonly agreed that GMR arises from spin-dependent scattering due to exchange interaction between conduction electrons and magnetic scattering centers. The magnitude of GMR directly depends on the strength of exchange interaction which in turn depends on the choice of constituents. The dimensional constraints and interface roughness of the magnetic component are also determining factors in the behavior of GMR. These factors are influenced by material growth processes, conditions, and post-deposition thermal annealing.

In this work we studied how the processing conditions affect the magnetotransport properties in two metallic granular systems, Fe-Ag and Co-Ag. The processing conditions include such factors as deposition rate, sputtering gas pressure, substrate temperature, and post-deposition annealing. We found that GMR is very sensitive to some fabrication parameters, in particular, to the deposition rate and annealing temperature. We investigated the effect of *in situ* annealing and compared it to post-deposition annealing results.

The Co-Ag samples were deposited on Si substrates by a single magnetron sputtering gun loaded with a composite target. The Fe-Ag samples were made by codeposition using cluster guns loaded with pure targets (>99.9%) of Fe and Ag. Typical samples were 5000 Å (Co-Ag) and 2500 Å (Fe-Ag) in thickness. For *in situ* annealing, the duration of heating and sputtering was about 15 min, about the same as the time of post-deposition annealing. Samples were deposited at ambient temperature (~50 °C), 200, 250, 300, 350, and 400 °C, with the same sputtering rate and gas pressure. For rate-dependence study sample depositions were done at ambient temperature (RT). All sample processing was carried out under a base vacuum of better than 1.0×10^{-7} Torr.

The standard photolithography and wet-etching technique was used to pattern the samples into a Hall bar configuration. This allowed us to simultaneously measure the resistivity and Hall resistivity. The Hall-effect measurement provides us with information of carrier density and type, as well as effective mean-free path.[6] In the transport measurements, the magnetic field was swept in a full circle (−8 T↔+8 T) to account for magnetic hysteresis effects. The hysteresis measured agrees with that determined by magnetic measurements, which were carried out in a superconducting quantum interference device (SQUID) magnetometer. Structural information was obtained by x-ray diffraction, transmission electron microscopy (TEM), and magnetic measurement. Detailed results are presented elsewhere.[7]

Figure 1 shows a typical measurement of magnetoresistance (MR) $\rho_{xx}(H)$ for a RT sample of $Co_{20}Ag_{80}$. Hysteresis is clearly observable with the MR maxima located at the coercive field H_c, where the magnetization of the sample reaches zero. There exist different definitions of GMR. In this work the GMR is defined as

$$\mathrm{GMR}=\Delta\rho/\rho=[\rho_{xx}(0\ \mathrm{T})-\rho_{xx}(8\ \mathrm{T})]/\rho_{xx}(8\ \mathrm{T}), \quad (1)$$

since at $H=8$T the MR is almost saturated.

Let us first pay attention to the effects of annealing. Under equilibrium Co or Fe is immiscible with Ag.[8] For the as-sputtered samples deposited at a moderate rate (~4.0 Å/s), the size of the magnetic particles is about ~20 Å as determined by TEM and magnetic measurements. Annealing

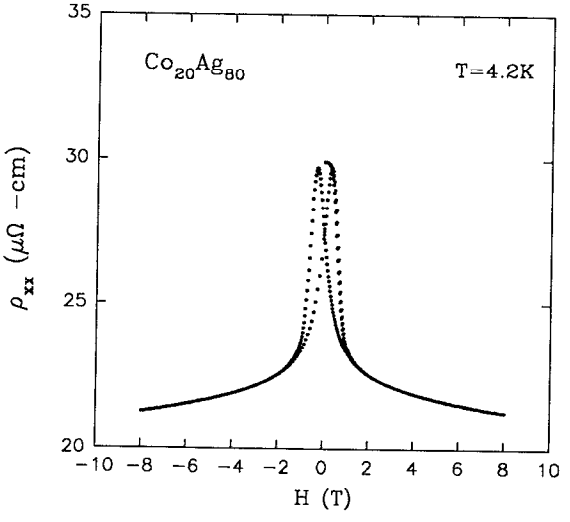

FIG. 1. Magnetoresistivity $\rho_{xx}(H)$ for $Co_{20}Ag_{80}$ deposited at ambient temperature with a rate of $R=4.0$ Å/s and $P_{Ar}=4.0$mTorr. $T=4.2$ K.

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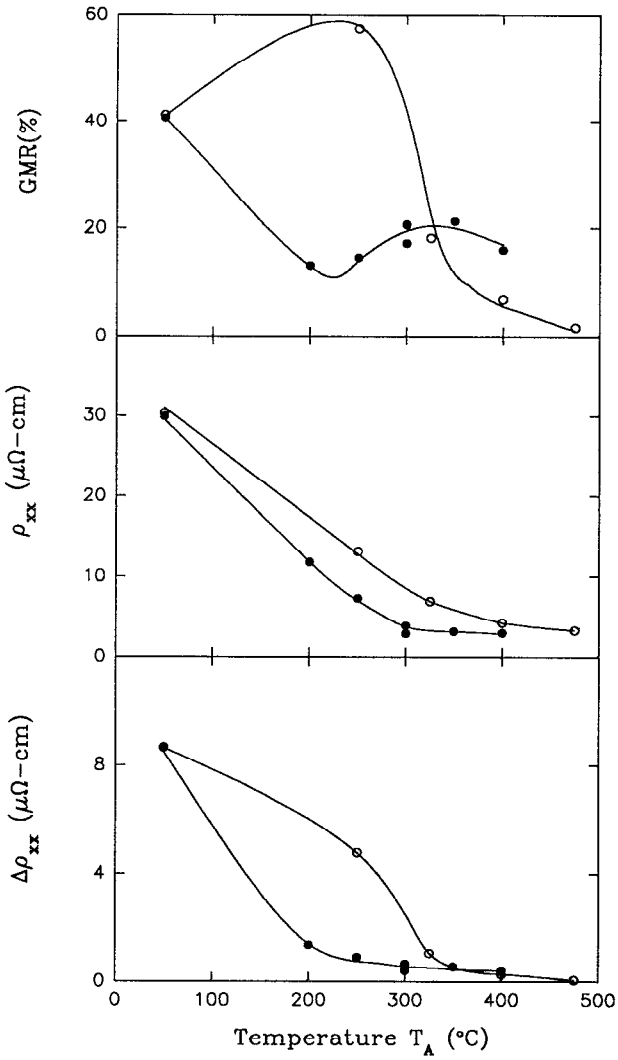

FIG. 2. GMR (upper), ρ_{xx} (middle), and $\Delta\rho_{xx}$ (lower) for $Co_{20}Ag_{80}$ samples (filled circles) deposited at various substrate temperatures, and for $Fe_{13}Ag_{87}$ samples (open circles) after post-deposition annealing at different T_A. Solid lines are guides to the eye. $T=4.2$ K.

increases the magnetic particle size and reduces disorder. For example, after post-deposition annealing for 15 min at 400 °C, the magnetic particle size increased to ~70 Å, whereas the zero-field resistivity ρ_{xx} decreased by one order of magnitude. ρ_{xx} contains contributions from magnetic and nonmagnetic scattering. Both are reduced by annealing. In granular materials, the magnetic spin-dependent scattering occurs primarily at the interface.[9] Thus if the magnetic scattering were dominant in ρ_{xx}, the decrease in ρ_{xx} would be much smaller (by about a factor of ~3) as a result of the reduced surface-to-volume ratio.

The effects of post-deposition annealing are demonstrated in Fig. 2. The measured GMR (upper panel), zero-field resistivity ρ_{xx} (middle), and the net change in resistivity $\Delta\rho_{xx}$ (lower) versus post-deposition annealing temperature T_A are presented for $Fe_{13}Ag_{87}$ samples as open circles. The results for $Co_{20}Ag_{80}$ and other granular systems are very similar.[6,10] GMR initially increases with annealing temperature T_A and subsequently decreases at higher T_A. But if ρ_{xx} and $\Delta\rho_{xx}$ are examined separately, both are found to monotonically decrease as T_A increases. The variation of GMR with T_A results from the difference in the rates of change of $\Delta\rho_{xx}$ and ρ_{xx}. In the low T_A region ($T_A<250$ °C), $\Delta\rho_{xx}$ decreases slowly, whereas ρ_{xx} decreases relatively quickly. This results in an initial increase in GMR. In the high T_A region, $\Delta\rho_{xx}$ drops very quickly over a narrow T_A range, and then monotonically approaches zero at 500 °C. The decrease in ρ_{xx} is, on the other hand, slow over the same T_A range. Hence the GMR shows the subsequent decrease in the high T_A region.

The observed variation in MR can be qualitatively explained as follows. $\Delta\rho_{xx}$ reflects the strength of the magnetic scattering. The structural characterization shows that the magnetic particle size increases slowly with T_A in the low T_A region. This results in a slow variation in magnetic scattering, and therefore in $\Delta\rho_{xx}$. The initial fast decrease in ρ_{xx} is mainly due to a decrease in the contribution of disorder and, to a lesser extent, magnetic scattering. In the high T_A region, magnetic particle size increases more rapidly with T_A. Other changes, e.g., interface roughness and particle shape, may also occur. The partial resistivity due to magnetic scattering is affected more strongly, resulting in a steeper decrease in $\Delta\rho_{xx}$ in the high T_A region. Disorder, being much reduced, becomes less sensitive to annealing.

Most studies so far have focused on the influence of post-deposition annealing on GMR. Little attention has been paid to the effects of growth temperature during thin-film deposition, i.e., *in situ* annealing, which affects the microstructure differently from post-deposition annealing. In Fig. 2, the filled circles represent the data of GMR, ρ_{xx}, and $\Delta\rho_{xx}$ for $Co_{20}Ag_{80}$ samples deposited at different substrate temperatures. It is seen that GMR suffers a large drop even at low T_A. At about $T_A\approx200$ °C, GMR reaches a minimum and then starts to develop a peak at $T_A\approx320$ °C. This behavior is substantially different from that of post-deposition annealing.

The cause for the above GMR behavior is again due to the rate of change of $\Delta\rho_{xx}$ and ρ_{xx}. Under *in situ* annealing, $\Delta\rho_{xx}$ decreases much faster with T_A than ρ_{xx} does below $T_A\sim200$ °C, resulting in the initial drop of GMR. However, between 200–300 °C, the rate of change of $\Delta\rho_{xx}$ slows down substantially, while the rate of change of ρ_{xx} remains about the same. This causes a temporary increase in GMR. Figure 2 shows that at low T_A, *in situ* annealing suppresses $\Delta\rho_{xx}$ much more efficiently than post-deposition annealing. This reveals the susceptibility of microstructural changes to *in situ* thermal annealing.

The appearance of a GMR peak at high T_A is very desirable from an application point of view. Samples made at higher T_A have substantially lower saturation field for GMR. The GMR value at the second peak is about a factor of 2 smaller than that of the as-sputtered sample. But the saturation field H_s has decreased by a factor of 5. We define H_s as the field at which 90% saturation has been achieved. We found that $H_s\approx3.1$ T for the RT sample, and $H_s\approx0.59$ T for samples annealed at 300–400 °C. Our study opens a new route in the search for the optimal condition for GMR effect.

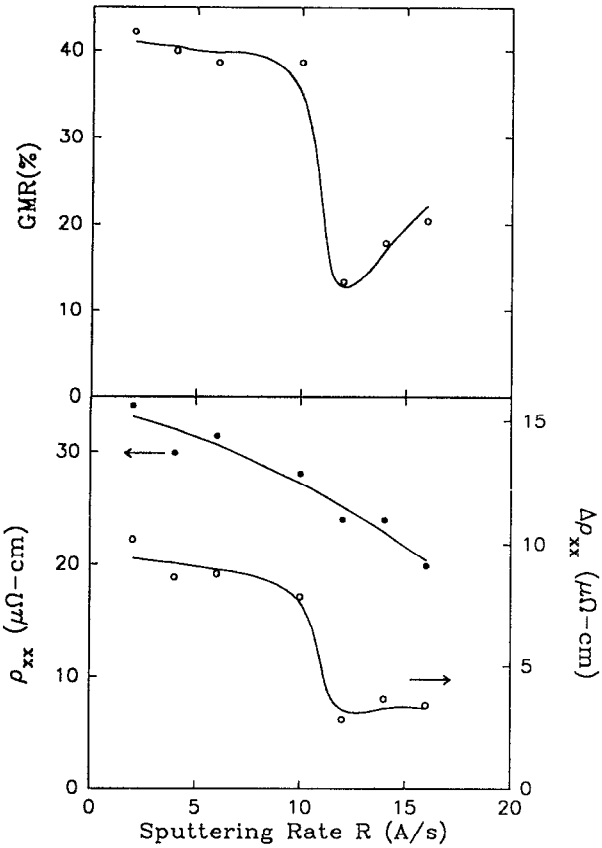

FIG. 3. GMR (top), ρ_{xx} and $\Delta\rho_{xx}$ (bottom) for $Co_{20}Ag_{80}$ samples obtained at different sputtering rates. Solid lines are guides to the eye. $T=4.2$ K.

In situ annealing could be more advantageous than post-deposition annealing.

Next we turn our attention to another processing parameter, i.e., deposition rate R. Different energies are carried by the deposited materials at various rates R. Thus different kinetics are involved in different rate regions. The measured GMR, ρ_{xx}, and $\Delta\rho_{xx}$ for $Co_{20}Ag_{80}$ as a function of R are presented in Fig. 3. GMR has its highest values (~40%) in the low R region ($0<R<10$ Å/s) and is only weakly dependent on R. But there is a sudden transition in GMR to a much lower value (~15%–20%) at $R\sim10$ Å/s. This transition marks the onset of microstructural change occurring in the high rate region.

Examining the variations of ρ_{xx} and $\Delta\rho_{xx}$ with R independently, we observe that the transition in GMR at $R\approx10$ Å is due to a large drop in $\Delta\rho_{xx}$. On the other hand, ρ_{xx} varies with R gradually, slightly decreasing as R increases. Thus the transition observed here is due to changes in magnetic arrangement in the samples deposited at high rates. This is presumably due to the higher kinetic energy carried by the deposited materials. Structural characterization showed that the Co particle sizes increased only slightly in the high R region, indicating that the particle size effect is unlikely to be the cause for the transition in GMR at $R\approx10$ Å/s. It is most likely due to changes occurred at the interface between the magnetic particles and Ag matrix.

It has been found that sputtering gas pressure induces changes in interface roughness and hence changes the size of GMR in multilayers.[11] We have investigated this possibility in our granular systems by varying the Ar gas pressure P_{Ar} from 2 to 8 mTorr. We found that the gas pressure has little effect on GMR and other magnetotransport properties in this pressure range.

In summary, processing conditions are very important in controlling the magnetotransport properties and GMR effect of metallic granular materials. A second peak in GMR at high annealing temperature is a unique feature to the *in situ* annealing. A substantially reduced saturation field coincides with this peak in GMR. We have also found a threshold in deposition rate, beyond which the strength of magnetic scattering, and hence GMR, suffers a precipitous drop. The different GMR behaviors between high substrate temperature and high sputtering rates are due to different microstructural changes in the systems. The former is mainly caused by an increase in particle size, whereas the latter is mainly due to changes in the magnetic structure at the granular interface. Among many processing parameters, only the sputtering gas pressure hardly affects GMR, ρ_{xx}, and $\Delta\rho_{xx}$.

We wish to thank Peng Xiong and Kent Ibsen for helpful technical assistance. This work was supported by National Science Foundation Grant No. DMR-9121747. G. X. wishes to thank the A. P. Sloan Foundation for a fellowship.

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