'Giant' magnetoresistance in obliquely co-evaporated Co–Ag films

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Magnetoresistance (MR) measurements at room temperature have been performed on obliquely (co-) evaporated Ag–Co films deposited at room- and elevated-temperatures. The 'giant' magnetoresistance ratio (max. 13% for a composition of about Co$_{85}$Ag$_{15}$) over a wide range of compositions has been measured. The films are polycrystalline and grown in a columnar morphology. The columnar diameter depends on the thickness and is < 20 nm at 400 nm thickness. From XRD, NMR and saturation magnetization ($M_s$) vs. at% Ag, one can conclude that the films consist of Co–Co and Ag–Ag clusters. The coercivity depends on the thickness of the films (100–700 nm) and varies from 5 to 15 kA/m.

1. Introduction

Since Baibich et al. [1] reported in 1988 on the 'giant' magnetoresistance (MR) effect in Fe/Cr multilayers, large effects were reported in other multilayer systems consisting of a ferromagnetic component and a conducting non-ferromagnetic component, but also in sandwich structures of, i.e., FeMn/NiFe/Cu/NiFe [2,3], and very recently also large effects have been discovered in so-called granular thin films [2–5] prepared by co-sputtering of ferromagnetic materials (Co, Fe, Ni, NiFe) and the non-ferromagnetic materials Ag and Cu.

These large magnetoresistance effects can be very interesting for sensor applications if the properties of the layers can be adjusted to what is needed. In granular films, one parameter affecting the magnetoresistance is the size of the ferromagnetic granules. The aim of this study is to show an alternative method, instead of sputtering from composite targets, to obtain small ferromagnetic clusters in a non-ferromagnetic matrix. The granularity of the sputtered films is based on the fact that the solubility of the ferromagnetic materials in the conducting material (Ag or Cu) is very small, allowing the formation of metastable alloys. A post-annealing treatment (at higher temperature) on these sputtered films leads to a diffusion process and consequently to a further precipitation of Co in the Ag or Cu matrix.

We introduce the oblique incidence vapour flux deposition method using opposing directions for the ferromagnetic and non-ferromagnetic materials by which the compositional separation of both materials is enhanced by the process itself.

Here we report about the preliminary results on composition, microstructure, magnetic properties and GMR values of oblique co-evaporated films of Co/Ag.

2. Preparation technique

A Leybold high vacuum system LH560 was used for co-deposition of Co and Ag under an angle using two e-beam guns. The two vapour beams arrive from opposite directions under the same angle. The basic geometry of the process is illustrated in Fig. 1.
The two e-beam sources are situated 268 mm from each other. The distance between source and substrate holder is 257 mm. The incoming angle for both materials is equal ($\alpha_{11} = \alpha_{12} = 27.5^\circ$). The angle of incidence is defined between the film normal and vapour flux direction. The substrate material used is Si(100) and the deposition temperature was either ambient (room) temperature (referred to as $T_r$ samples) or high (referred to as $T_h$ samples). In the latter case, the temperature near the heater was 400°C. The substrate temperature, measured by means of a thermocouple in contact with the back of the Si substrate, was lower than this heater temperature. The lowest back pressure in the turbo pumped system was about $10^{-7}$ mbar.

The total deposition rate (Co + Ag) was varied between 3.5 and 12.8 Å/s. The separate deposition rates of both sources during deposition were monitored by calibrated quartz crystal oscillators. The thickness of the layers was between 81 and 706 nm. The deposition rates of Co and Ag were, respectively, 1.4–4.2 Å/s and 0.8–7.6 Å/s. As source materials, we used 99.99% purity Co and Ag. The composition of the films varied between 34.9 and 84.2 at% Co.

With the substrates in the middle position (see Fig. 1) between the two sources, the two vapour fluxes overlap each other. Since the two separate directions are intended to arrive at the growing film surface from opposite directions, it is important that this overlapping does not have too much effect on the vapour impingement. In the experimental situation, the background pressure was sufficiently low and caused no significant deterioration of the vapour flux direction.

For various types of material, the two separate sources of vapour flux can yield a special type of compositional separation (CS), the so-called process-induced compositional separation, which is closely related to the evaporation geometry.

The use of this technology for compositional separated films has been proved by using this method for preparing Co–Cr films not only for perpendicular magnetic recording [6–8] but also for other applications [9,10]. The results presented in this paper are based on a systematic research on obliquely (co-)evaporated Co–Cr media for magnetic recording applications. The relations between deposition parameters, morphology, texture and magnetic behaviour of this type of thin film have been studied in our group in the past 5 years [6–8,11,12,17,19]. From this study we learned, from experimental data obtained by various methods and techniques, that in the case of Co–Cr even at ambient temperature a compositional separation takes place. In the case of evaporation, the film temperature is much lower than the ambient sputter temperature due to the difference of particle energies. In both cases, deposition at an elevated temperature or an annealing step after deposition can give a more pronounced compositional separation.

The data obtained from Co–Cr was the inspiration to try also Co–Ag because it is known that these materials will hardly form an alloy. This fact in combination with the deposition technology at ambient temperature should give us probably a more separated Co and Ag phase. This is of course also dependent on the angle of incidence and the proportion of Co to Ag. So we expected to tailor the local chemical composition in the case of Co–Ag in a better way than in the case of Co–Cr. Last but not least we found by NMR experiments [16] that compositional separation has occurred in Co$_{42}$Ag$_{58}$ films. After annealing at successive steps of 225, 325 and 425°C, each for 2.5 h, the compositionally separated state developed even more; in the NMR spectrum only the pure Co component was present.
Magnetic properties have been determined by VSM and torque magnetometer while the MR measurements were carried out by a four-point in-line probe with both voltage and current (of 1 mA) in plane of the film. Structural and compositional analysis have been carried out using XRF, XRD and SEM. All measurements have been carried out at room temperature.

3. Driving forces of compositional separation (CS)

Compositional separation in Co-Ag films effectively means chemical non-homogeneous distribution of Co and Ag in the lateral direction. It considerably influences the magnetic behaviour of the films and it is therefore one of the most important structural features. Unfortunately, it is also a difficult phenomenon to characterize, mainly because of the small dimensions of the final morphology of the deposited layers (see below).

Two very useful and clear distinctions can be made to understand the mechanism of CS, namely:

(1) there is a driving force related to the process geometry of the two opposite vapour flux directions of the two materials used [11,12] in our case Co and Ag;

(2) there are driving forces related to the deposition temperature which can be defined as thermally enhanced CS, which are not restricted to the technology used in this work. One can find this mechanism also for sputtered, evaporated and electroplated plated thin films.

Hereafter some more attention will be given to the ideas behind the process-induced CS. An ideal representation of the process is given in Fig. 2.

The geometric effect is due to the shadowing mechanism [13] because the Co and Ag atoms have shadowed areas that are positioned opposite to each other. The most likely impingement place for Ag is, at every stage of film growth, in the shadowed area of the Co vapour and especially on one side of the tilted columns and in case of a high percentage of Ag, and vice versa. The amount of tilting of the columns and the related oblique top of the columns count significantly in this matter. If the adatoms have limited mobility (at low temperature) then they will stick at a position very near to the initial impingement place. This can lead to the process-induced CS, where one side of the columns is Ag-rich. In order to have such a geometrical effect, it is essential that the two vapour beams are really coming from separate directions and that no mixture of directions is formed in the overlapping part of the flux. Also the background pressure is important, because a residual gas will interfere with the vapour flux and make its direction less distinct.

To see whether two metals will form an alloy, the ‘heat of formation’, which is formulated in the Miedema model [14], can be used as an indicator. When the heat of formation is negative, energy is freed upon alloying. Miedema’s calculations resulted in a fast graphical method (alloying diagram) to see if two metals will alloy or not. It appeared that Co will not alloy with Ag (and Cu and Au).

This fact and the deposition technology used can give us separated Co-rich and Ag-rich areas.

4. Structure and morphology

Two of the thickest samples (700 and 400 nm) containing 55 and 59 at% Ag were examined with SEM in cross-section parallel to the evaporation plane (see Fig. 3).
A columnar structure is present and tilted about 10° towards the Ag source direction. This is obviously the result of the higher at% Ag than at% Co in the film. The columnar size is very small (for instance much smaller than Co–Cr samples made under the same conditions), namely < 20 nm for 400 nm and < 30 nm for 700 nm thick layers. From many studies in the literature, it is known that, in the case of sputtering and evaporation, materials tend to grow in a columnar shape. In the case of oblique evaporation, the columnar growth is mainly promoted by the shadowing mechanism. Depending on the substrate conditions, one can find that a columnar diameter grows as a function of the thickness of the layer. In the case of Co–X compositions (X = Cr, Ta, Ag), we found this effect during sputtering and evaporation. By using a seed layer, this effect is drastically reduced and in certain combinations the columnar diameter can be determined as constant over the layer thickness. Influences from bias, sputtergas and substrate temperature can be
clearly seen. The nucleation and growth process is responsible for the final growth of the layer. The columnar diameters (d) as a function of the layer thickness (t) of Co–Ag films are: t = 100 nm, d = 7.5–15 nm; t = 250 nm, d = 12.5–25 nm; t = > 400 nm, d = 15–35 nm. For higher substrate temperature (about 250°C), we found: t = 250 nm, d = 12.5–30 nm; t = 400 nm, d = 15–50 nm; t = 750 nm, d = 15–110 nm. Compared with sputtered Co–Cr films, the columnar diameter is rather small (for instance t = 600–700 nm, d = 100 nm). The difference is mainly attributed to the higher surface temperature during the growth of the film.

Although there is an increase in columnar diameter with increasing film thickness in the oblique-evaporated Co–Ag films, it is much smaller than in the case of sputtered layers and layers evaporated at higher substrate temperature. It can be explained qualitatively by two facts, namely the small increase of layer temperature during growth, and the deposition time for the 700 nm thick layer is about two times more that for the 400 nm layer (about 140 s instead of 80 s). During this deposition trajectory, the substrate temperature is still increasing and this can have an influence on the columnar diameter growth.

Furthermore, the texture of the layers is strongly (111) oriented. In the fcc case, this is the most favourable crystal plane and in terms of the ‘survival of the fastest’ growing mode this can cause an increase of the diameter.

Surface SEM observations however revealed larger particles on the surfaces. This surface topology does not seem to consist of columnar tops; instead it is likely to consist of oxidized or sulphide particles, and Ag compounds are known to form easily. A simple observation of a fresh deposited sample and a two month old sample shows that the latter had a larger amount of the larger and protruding particles. Further analysis of the morphology and chemical (surface) composition will be carried out.

From XRD measurements, we can conclude that the Co–Ag films are polycrystalline and consist of two separate lattices. The Ag sub-lattice is fcc and the Co lattice is either hcp (13–16 at% Ag) or fcc (> 31 at% Ag).

The hcp structure of the lower at% Ag samples have the lattice data of d_{002} = 2.036–2.040 Å, a = 2.495–2.503 Å and c/a = 1.630–1.632. Furthermore, the (111) Ag lattice spacing is around 2.32–2.34 Å and also a reflection probably from Ag_2S_2O_7 was measured.

For the > 31 at% Ag, a separate fcc Co and fcc Ag lattice have been measured. Both lattices have their (111) planes parallel to the film surface and consequently have a texture axis, being [111]

![Fig. 4. An XRD scan showing two separate peaks for Ag and Co both from fcc (111) planes. The peak at 2θ = 33° is from the Si substrate.](image-url)
perpendicular to the surface. The Co(111) lattice spacing is larger than for pure fcc Co and it increased with Ag content and decreased with deposition temperature. Measured values are: 2.058 Å (35 at% and room temperature ($T_r$) deposited), 2.058–2.076 Å (50–60 at%, $T_r$) (see Fig. 4) and 2.054 Å (61 at%, high temperature). Furthermore, the (111) Ag lattice spacing is smaller (2.332–2.338 Å at $T_r$) than for pure fcc Ag (2.539 Å). It increased at higher deposition temperatures (2.344 Å). The XRD pattern agrees well with the sputtered Co–Ag film at a substrate temperature of 100°C of Liou et al. [18].

The $\Delta \theta_{50}$ of the Co(111) is about 16° and for the Ag(111) about 19°. After an annealing step of 225, 325 and 425°C (each step 2.5 h at $10^{-4}$ Pa), the higher Ag content samples changed from fcc into a mixture of hcp Co and fcc Ag.

5. Magnetic analysis

The magnetoresistance as a function of the film composition is given in Fig. 5. The resistance of the film is measured to a maximum field of 960 kA/m. The films were not saturated at this field. A typical curve is shown in Fig. 6. The MR is calculated as the difference of $R$ at zero field and maximum field divided by the $R$ at zero field ($\frac{(R_0 - R_{\text{max}})}{R_0} \times 100\%$). Although there is a large variation in the thicknesses of the films, it seems that this has not much effect on the MR. The MR is measured in three directions:

(i) current parallel to the transversal plane, that means perpendicular to the plane of incidence (TM direction) and the magnetic field in plane;

(ii) current parallel to the incidence plane (LM direction) and the magnetic field in plane;

(iii) current in the LM direction and the magnetic field perpendicular to the film plane.

There is not much difference in the measured values; the resistance in the LM direction seems to be a bit larger than found in the TM direction, probably due to the open regions between the columns caused by the shadowing effect in that direction in the film.

Although we did not measure a maximum due to lack of films in the lower Co region, it seems that the curve we find compares quite well with what is found for sputtered films (in the same thickness range) by Barnard et al. [2] although the position of the maximum in our films seems to coincide with the position found for the thicker (also sputtered) films made by the same group [15]. Films deposited at a higher substrate temperature gave a higher value for the MR as films deposited at room temperature, probably due to

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**Fig. 5.** The magnetoresistance ($\Delta R / R$) as a function of the Co concentration.
the higher mobility of the atoms which will cause a better separation of the Co and Ag.

Due to the evaporation geometry and the growth mechanism we obtained a different morphology for the different in-plane directions in the film. In the incidence (LM) plane, the columns are separated by open regions due to the shadowing effect. In the plane perpendicular to the incidence plane (TM), where the vapour supply is homogeneous and the shadowing effect is not present, clustering of columns (bundling) can occur under certain deposition conditions. Magnetically this structural difference shows only in a difference in coercivity for the LM en TM planes. In Fig. 7, VSM hysteresis loops measured in the LM direction are shown, which compare very well with the loops measured in the TM direction, except that the $H_c$ is higher in the LM direction for the in-plane loops (Fig. 8).

In Fig. 8 the coercivity measured in the LM and the TM direction is given as a function of the film thickness. In general the coercivities measured in plane (both LM and TM direction) and perpendicular to the film surface have very low values: for a 200 nm thick film about 10 kA/m with a slight dependence on the composition. It can be concluded that the films are more or less isotropic. The slightly higher $H_c$ for thicker films can probably be related to the larger columns.

In Fig. 9, the saturation magnetization ($M_s$) is shown as a function of the average at% Ag. As can be seen, the $M_s$ decreases almost linearly with increasing Ag content. In order to exclude a mere dilution effect, a correction is made for non-magnetic volume under the assumption of complete separation of Co and Ag. The calculated $M_s^*$ is also given in Fig. 9.

With a non-homogeneous distribution of Co and Ag, a deviating relation between $M_s$ and the average content of Ag occurs. The Co volume can be calculated in two different ways. First by using the densities and second by taking the atomic radii. Both methods give within 1% the same result. Here the atomic radii are used. If in our films Co and Ag are assumed to be completely separated, the resulting ferromagnetic film volume ($V^*$) is related to the total volume ($V$) through

$$V^*/V = A/(A + B)$$

with $A = 4/3 \pi r_{Co}^3 N_{Co}$ and $B = 4/3 \pi r_{Ag}^3 N_{Ag}$.

In this expression the radii of the atoms are denoted as $r$ and the number of atoms as $N$, both with subscripts for Co and Ag. The $M_s^*$
under complete separation conditions, $M_s^*$ can then be calculated by

$$M_s^* = M_s V/V^*$$

$$= M_s (1 + \text{at\% Ag} \cdot r_{Ag}^3 / \text{at\% Co} \cdot r_{Co}^3).$$

Here $M_s$ is the saturation magnetization if the total film volume would be ferromagnetic. Effectively this comes down to excluding the dilution effect (in clusters) that Ag is supposed to have on Co. If the films consist of Co clusters on one side and Ag on the other side of the columns, then this dilution is merely a volume effect and $M_s^* (\text{at\% Ag})$ should be constant. If Ag is to some extent also present within the Co matrix, then besides the volume effect it also reduces the number of Co–Co neighbours. The exchange energy between neighbouring atoms and the Curie temperature of the film are hereby reduced.
In that case $M_s$(at% Ag) decreases more strongly than in the case of separation into merely clusters and $M_s^*$ (at% Ag) remains a decreasing function.

At low Ag content, the calculated saturation magnetization ($M_s$) is almost constant with an increasing amount of Ag. This indicates that, at low Ag compositions, $M_s$(Ag) is dominantly decreased by mere dilution effect of Ag–Ag clusters. The fact that the extrapolated value of $M_s$ is not yet zero at 80 at% Ag (and thus not only a decrease of exchange moment occurs due to fewer Co–Co neighbours) supports this. Thus, Co and Ag have been separated and compositional separation occurred in those samples co-evaporated at room temperature. In the high Ag content region, $M_s$ decreases with an increasing amount of Ag, as does $M_s^*$. The decrease of $M_s$ with average Ag content tends to be less than is expected for a homogeneous dilution effect (the slope through the datapoints is less steep). Another possible reason for the weaker decrease of $M_s$ (%Ag) is an electron sharing of Co and Ag. Possibly an 'electron transfer' of Co to Ag occurs, since Ag is the more noble metal of the two. A different polarization mechanism takes place in Co/Pd multilayers. However, the electron transfer from Co to Ag is less likely than the occurrence of Co–Co clusters and, if it should take place, then it is probably a minor effect. Furthermore, the presence of Co-rich regions is proved by NMR measurements. It is also most likely because of the compositional separation.

Another argument for the decrease of $M_s$ at high Ag at% at room temperature is probably due to thermal relaxation in small Co clusters. Temperature dependent measurements should be carried out to clarify this point.

6. Discussion and conclusions

In as deposited Co–Ag films, two separate lattices are present. At higher substrate temperatures, the lattice parameters for fcc Ag and fcc Co get closer to the pure metal lattice parameter. Clearly CS with regions existing of Co–Co clusters and Ag–Ag clusters, but also Co-rich regions with some amount of Ag in it, are present. This has also been confirmed by NMR experiments. By preliminary NMR experiments we have shown that, for (Co–Cr and Co–Ag) films deposited at room temperature, the number of Co–Co clusters has increased after an annealing treatment is carried out [16,17]. After annealing, an hcp Co structure is present.

At low at% Ag, the $M_s$ vs. at% Ag decreases according to a 'nearly-merely' volume dilution and $M_s^*$ vs. at% Ag is nearly constant. $M_s$ is not yet zero at 80 at% Ag.

The samples deposited at elevated substrate temperature have a slightly higher $M_s$ than the low temperature samples and the $M_s$ increases after an anneal step. Since the solid solubility for Co and Ag is very small, an amount of extra energy can increase the separation between them. In that case, the Ag in the Co matrix can diffuse to the Ag clusters, whereby the number of Co–Co neighbours is increased, which is supported by also NMR experiments.

The MR effect we found in our films compares well with sputtered film in the same thickness range [15], although the maximum effect occurs at a slightly different composition. It is not clear what the role is of the different processes, causing the separation of the Co and Ag. More work has to be done in order to obtain a better understanding of these mechanisms.

References


