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Tunneling magneto-resistance granular thin films deposited by thermo-ionic vacuum arc technique

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Co-MgO granular films presenting TMR effects were prepared by thermo-ionic vacuum arc method with the simultaneous ignition of plasma in Co and MgO vapors. Morphologic, structural and magnetic behaviors were analyzed in as prepared and annealed samples. The influence of the Co content on the magnetic properties of the prepared films was analyzed, in correlation with tunneling magneto-resistance effects. The tunneling magneto-resistance effect is maximal for certain Co content. This behavior was interpreted by the contrary effects of decreasing the average size of the magnetic grains, and hence the average inter-grains distance at higher Co relative content, and the enhanced magnetic disorder in very fine grains dispersed in the insulating matrix.

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1. Introduction

Granular thin films for tunneling magneto-resistance (TMR) applications can be made of 3d magnetic metal (e.g. iron, nickel or cobalt) clusters, uniformly distributed within an insulating matrix (e.g. magnesium or aluminum oxide). These films are able to provide both positive and negative electrical resistance variation under the influence of an external magnetic field. Due to the presence of the insulating matrix, the electrical resistance of such nanostructures is much higher than that of similar GMR structures with magnetic clusters dispersed in conductive matrix. By similitude with layered systems, a much enhanced magneto-resistive effect would be also expected, making such structures more attractive for applications as magnetic memories or sensitive magnetic field sensors. In a layered system, the magnetoresitance coefficient, MR(θ), depends on the angle θ between the magnetic moments of the ferromagnetic layers sandwiching the dielectric layer, by (1-cos θ)/2 (in turn, angle θ depends on the magnetic field applied to the system). The proportionality coefficient is $TMR=(R_a-R_p)/R_p$, with R_a and R_p the resistances of the system in anti-parallel and parallel configuration of the ferromagnetic layers. This proportionality coefficient depends in a specific way on the geometrical/ structural parameters of the TMR structures [1, 2]. In the Julliere's simplified model [3], only the spin polarizations of the conduction electrons in the two electrodes influence the TMR coefficient. Electrons with a certain spin orientation in the first electrode should find empty states of similar spin orientation in the second electrode, in order to enhance the tunneling probability [4]. However, the spin polarization of the tunneling current between the ferromagnetic electrodes is extremely sensitive to surface and interface properties because of the short coherence length characteristic of the ferromagnetic state. Similitude with the case of TMR multilayered systems can be found also in the case of nanoglobular systems. The advantages are mainly related to the simplicity of the system and hence with the high productivity and lower production costs of such structures. The disadvantages are related to the more complex physics behind the systems, related to both the imperfections of the large interface between the magnetic nanoparticles and the dielectric structure as well as to the much more complex magnetic configuration of the nanometer-size magnetic grains. In the case of a nanoglobular system, the electrons will become spin polarized in the first magnetic cluster. Their associated wavelengths should tunnel towards a neighboring cluster with empty density of state of similar spin polarization and parallel orientation of the magnetic moment. The magnetic configuration of the ferromagnetic nanosized clusters is of main importance, but their response to an applied field is not so straightforward, due to their size distribution, possible intergranular couplings, possible superparamagnetic effects or impurities/ nonstoichiometry near the interface of the ferromagnet/dielectric phases. This paper reports on structural, magnetic and tunneling magneto-resistance effects in granular systems obtained by thermo-ionic vacuum arc (TVA) method.

2. Experimental

The materials used for the combined simultaneous deposition were cobalt, as magnetic material, and MgO, as insulator. The TVA deposition method is described elsewhere [5]. In principle, it is based on the intense evaporation of the depositing materials placed in crucibles of high positive potential (anodes), under the bombardment of electrons emitted from a heated cathode filament. The evaporated particles are ionized and a high potential (some hundred of volts) low current (around one ampere) plasma is formed around the anode. The plasma

expands further in the neighborhood high vacuum space, where the grounded supports for sample preparation are mounted. The ions coming from different crucibles are simultaneously deposited on the substrates, giving rise to well structured and compact thin films. This method is efficiently in principle only for deposition of conducting materials, but we have proved out that some insulating materials (like MgO), can be also deposited, due to the fact that they become conductive when heating at high temperatures. Moreover, the obtained deposited layer preserves the electrical insulating characteristics of the bulk material, as proved by electrical measurements.

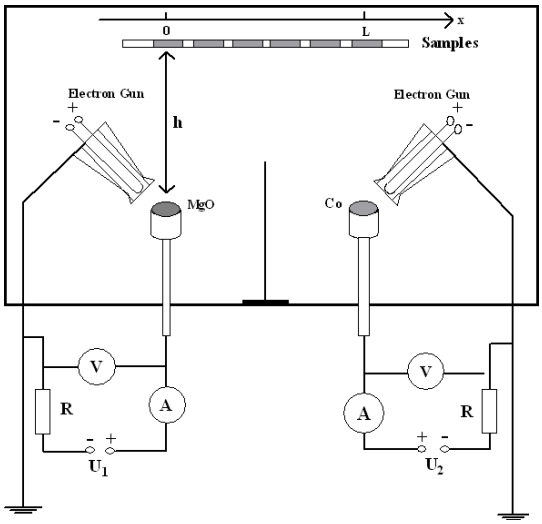

Fig. 1. A schetch of the experimental set-up for the simultaneous deposition of Co and MgO.

The experimental arrangement for processing TMR nanoglobular thin films is presented in Fig. 1, where two simultaneous discharges (one in cobalt vapors and the other in MgO vapors) can be induced in the high vacuum chamber (under 10^{-5} torr). An electrical screen has to be mounted between the two discharges in order to avoid their mutual influence and to maximize the simultaneous deposition of the neutral particles together with their ions. It is worth to mention that in this geometrical arrangement, the concentration of the magnetic metal in the MgO dielectric matrix will expectedly increase continuously with x (for x<L), due to the different distances of the substrates to the two anode positions (e.g. the sample placed at x=L will be just in the front of the Co crucible and hence will present the maximum amount of Co). The film substrates were $1cm^2$ rectangular pieces of industrial glass. The composition of the obtained nanogranular films was analyzed by Energy Dispersive X-ray (EDX) measurements, the film morphology and structure by Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM) and the magnetic properties were monitored via Magneto-Optic Kerr Effect (MOKE). Finally, the structural and the magnetic properties have been correlated with electron transport properties and TMR effects measured via the four point method with current in plane geometry.

3. Results and discussions

The relative amount of Co (at. %), as obtained by EDX measurements on different samples, versus the distance from the Co crucible to the film supports, is presented in Fig. 2 (e.g sample P3 corresponds to a distance of 28 cm whereas sample with the highest index number, P7, is the sample placed at x=L and corresponds to a distance Co crucible- film substrate of only 20 cm).

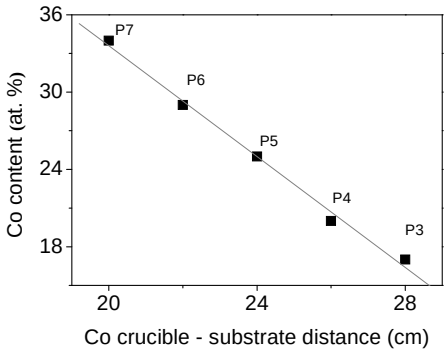

Fig. 2. The Co concentration against the distance between Co crucible and the film substrate.

One can observe the almost linear decrease of the cobalt concentration with the distance between the film substrate and the Co crucible (the lowest distance corresponds to the larger x and vice versa). As a consequence of the different Co contents in the different samples from P3 to P7, one can study the dependence of the TMR effect and the related structural and magnetic behaviors, versus the concentration of the magnetic element. It is worth mentioning that the thickness of the central sample, P_5, is 250 nm and the other samples present thicknesses of the same magnitude inside the measuring error bars. The variation of the TMR effect at room temperature (RT) versus the relative content of cobalt in the magnesium oxide dielectric film is shown in Fig. 3.

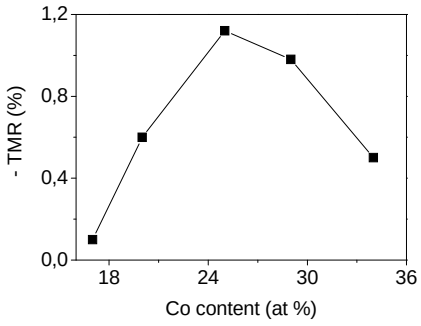

Fig. 3. The room temperature TMR effect for different Co concentrations in the MgO films.

It is easily observed that the TMR effect has a maximum value at a given Co concentration (26 at% in this case) and decreases much faster at lower Co concentration as compared with the case of higher Co concentrations in the range from 17 to 34 at %. Assumable, this effect has to be related with different morphology or size distribution of the Co particles in the dielectric matrix and we will return back to this point after presenting structural and magnetic data.

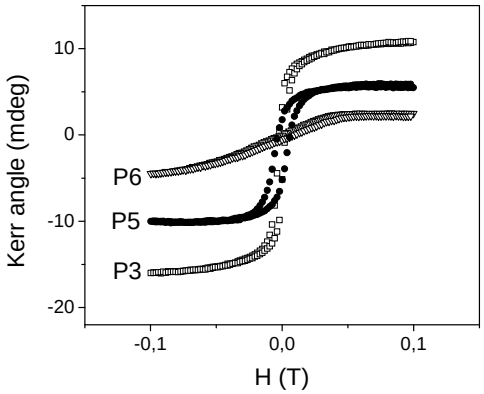

Fig. 4. Room temperature MOKE measurements on sample with increasing Co content.

The MOKE hysterezis loops obtained at RT on samples of different Co contents are presented in Fig.4. It might be observed that the magnetization in 0.1 T decreases continuously with the Co content. In order to get an hint about the correlation between TMR effects and magnetic data we will present in the following some structural and magnetic aspects of sample P5, showing the highest TMR effects. Both the as prepared sample, as well as an annealed P5 film processed by a post-deposition thermal treatment, performed at 300 ^{o}C for one hour in high vacuum condition (10^{-5} torr), were analyzed.

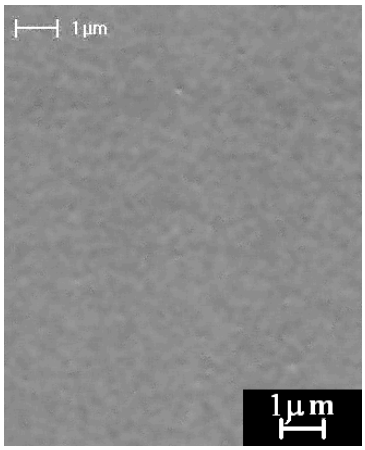

Fig. 5. SEM image of the surface morphology of the as deposited P5 sample.

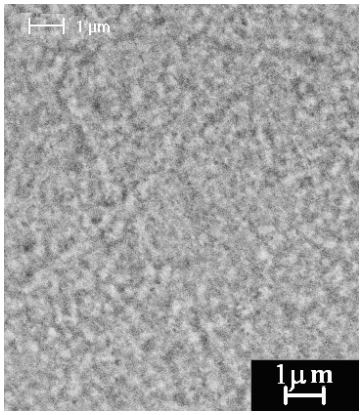

Fig. 6. SEM image of the surface morphology of the annealed P5 sample.

The EDX spectra collected on the two samples have shown slightly increased oxygen content in the annealed sample as compared with the as prepared one, which will lead presumably to an increased partial oxidation of the Co particles in the annealed sample. The SEM images of the as deposited and the annealed P5 films, presented in Fig.5 and Fig.6, evidence clearly much larger grains induced by the thermal treatment. HRTEM images of the as prepared and the annealed P5 films are shown in Fig. 7 and Fig. 8, respectively.

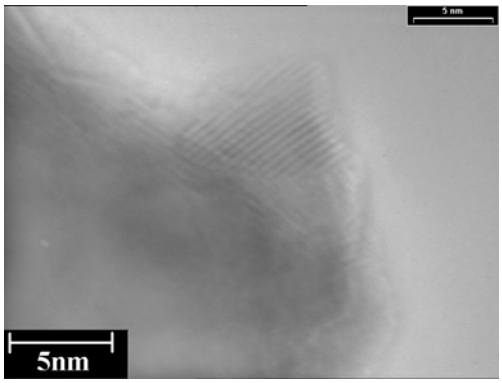

Fig. 7. TEM image of the as deposited P5 sample.

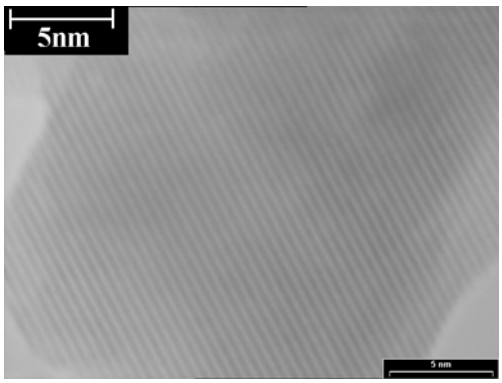

Fig. 8. TEM image of the annealed P5 sample.

Electron diffraction patterns evidence that the nice structure with well arranged atomic planes belongs to metallic Co grains, which dimensions are much larger in the thermally annealed sample as compared with the as prepared one. In addition, the electron diffraction has proven the presence of cobalt oxide (the antiferromagnetic Co_3O_4) in both the as prepared sample and the annealed. The amount of the cobalt oxide is slightly larger in the annealed sample, in agreement with the EDX data proving increased oxygen content in this sample.

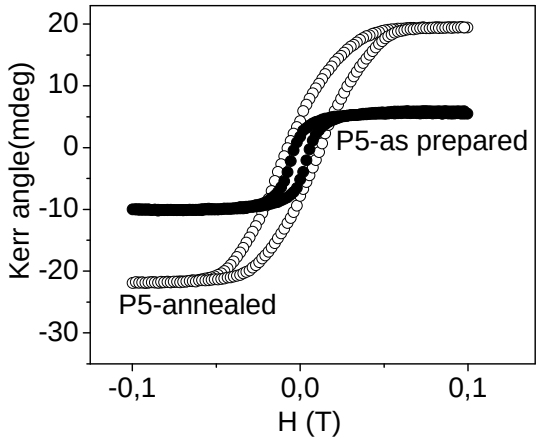

Fig. 9. Room temperature MOKE measurements of the as prepared and the annealed film P5.

The RT MOKE hysteresis loops of the as prepared and annealed P5 films are presented in Fig.9. One can see that the thermal treatment increases the saturation magnetization of the film as well as its coercive force. Based on this structural/morphologic picture of the two samples, we can interpret the corresponding RT MOKE curves as follows. In the as prepared sample, there are formed very fine Co grains (about 5 nm) with a thin magnetic dead layer of cobalt oxide, giving rise to a reduced magnetization of the sample (due to both defected spin structure and possible superparamagnetic behavior of the grains of lower dimensions). After the annealing treatment, the initial clusters agglomerate giving rise to much larger Co particles. In spite of a slightly thicker cobalt oxide layer on the surface, the Co core is significantly larger than in the case of the as prepared film, which leads finally to higher average magnetic moment per Co atom, due to both a less defected magnetic structure and reduced magnetic relaxation of the Co particles. Hence, a higher magnetization and coercive field is expected for the annealed sample.

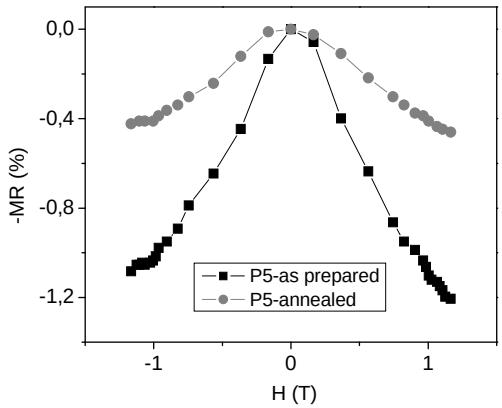

Fig. 10. TMR curves of the as deposited and annealed P5 nanoglobular films.

The field dependent TMR curves obtained at RT on the two P5 films (before and after annealing) are shown in Fig. 10. A much increased absolute value of the TMR effect has to be mentioned for the as prepared sample, in comparison with the annealed one. That is certainly due to increased distances between the magnetic grains in the annealed samples (directly connected with formation of much larger magnetic grains), diminishing drastically the tunneling probability in this system. However, the thermal treatment appears to decrease the TMR coefficient in Co-MgO systems, opposite to the effect of similar treatments applied to nanoglobular GMR systems like Co-Cu or Fe-Cu [6].

The above observation can be also extended to the case of the MOKE and TMR data presented in Fig. 4 and Fig. 3, respectively. The continuous decrease of the magnetization in 0.1 T with the Co relative content in the films has to be explained by a reduced average size of the Co grains (and implicitly by an increased particle density) in films of higher Co content. That would explain the fast increase of the TMR effect when increasing the Co content in the film up to the optimal value of 26 at. %. However, by further increasing the Co content, the TMR effect starts to decrease, due to an enhanced magnetic disorder specific to the very large surface area of very fine particles, connected also with a very weak magnetic response to the applied field.

4. Conclusions

Co-MgO granular films presenting TMR effects were successfully prepared by the TVA method. This was possible due to the conductive behavior of the MgO at high temperature, allowing so to ignite the plasma in the MgO vapors. Simple MgO thin films preserve the insulating electrical characteristics of the bulk material. Co-MgO thinn films with different Co contents were obtained by fixing film substrates at different distances from the Co and MgO sources. A maximum TMR effect of about 1% was obtained at room temperature for a relative content of 25 at. % of Co. High resolution TEM

and electron diffraction measurements reveal the presence of the Co grains as well as surrounding shells of cobalt oxide. Post deposition thermal treatments of the Co-MgO films (for one hour, at 300 C, in 10-5 Torr) increase substantially the average Co grain size and slightly the thickness of the cobalt oxide layers around nanograins. These structural results support the increased magnetization in the room temperature MOKE hysterezis loop in the annealed samples as well as the decreased TMR effect, due to increasing distances among Co nanograins.

The proposed processing method (TVA) allows the fast deposition of TMR granular structures with a large variation of the concentration of the magnetic metal in the insulating matrix. However, the TMR effects in such systems are still to low and further work is necessarily in order to improve them.

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References

[1] Li Xi et al. J. Phys. D: Appl. Phys. **33**, 621 (2000).
[2] J. S. Moodera, R. H. Meservey in Magnetoelectronics, Edited by M. Johnson, Academic Press, Dec 2004.
[3] M. Julliere, Phys.Lett., **54** A, 225 (1975).
[4] E. Y. Tsymbal, O. N. Mryasov, P. R. LeClair, J. Phys.: Condens. Matter **15**, 109 (2003).
[5] V. Kuncser, I. Mustata, C. P. Lungu, A. M. Lungu, V. Zaroschi, W.Keune, B. Sahoo, F. Stromberg, M. Walterfang, L. Ion, G. Filoti, Surf.& Coat. Techn, **200**, 980 (2005).
[6] A. Anghel, C. P. Lungu, I. Mustata, V. Zaroschi, A. M. Lungu, I. Barbu, M. Badulescu, O. Pompilian, G. Schinetie, D. Predoi, V. Kuncser, G. Filoti, N. Apetroaei, Czech J. Phys. **56**, B16 (2006).

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