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Cobalt ferrite thin films deposited by electrophoresis on p-doped Si substrates

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Abstract. The structural and magnetic properties of cobalt ferrite ($CoFe_2O_4$) thin films deposited by electrophoresis on p-doped Si(001) substrates have been characterized. The films were polycrystalline and composed by cobalt ferrite with the cubic spinnel structure. The observed decrease of the coercive field with the sixth power of the grain size was indicative of a competition between the magnetocrystalline anisotropy and the exchange coupling energy, on these randomly oriented nanosized grained films.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) thin films have recently been attracting much attention due to their high degree of multifunctionality [1-4]. Owing to the high coercivity of $CoFe_2O_4$, its high magnetocrystalline anisotropy and moderate saturation magnetization [5], as well as its good chemical stability and mechanical properties, these films are good candidates for applications in magneto optical devices [4] or high-density recording media [2]. Additionally, $CoFe_2O_4$ has also recently been proposed for application in magnetoelectric composite devices due to its high magnetostriction [1,3].

Cobalt ferrite films have been prepared by sol-gel [6], sputtering [7], laser ablation [8,9] or atomic layer deposition [10]. Recently, the electrophoretic deposition technique (EPD) has been employed for the production of functional thin films due to its versatility for application with different materials and the ability to be scaled-up to large volumes and sizes [11,12]. In EPD, two electrodes are placed inside a fluid with suspended charged particles (metals, polymers, ceramics or glasses). Then, when an electric field, is applied, the suspended particles move toward the oppositely charged electrode, where they accumulate and are deposited to form a film. After the deposition, a heat-treatment step is normally needed to further densify the film and eliminate porosity.

The deposition of ferrite films by EPD has been previously reported [13-14]. However, the influence of preparation conditions on the magnetic properties of the films, in particular of the heat

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treatment step, has not been fully characterized. Thus, here, cobalt ferrite thin films have been deposited by electrophoresis and the influence of the annealing process on the magnetic properties of the films was characterized.

2. Experimental

In order to form the electrophoretic suspension, a $CoFe_2O_4$ powder with average particle size in the range 35nm - 45nm was dispersed in 1-Octanol, with a concentration of 75 g/l. A small amount of iodine, with concentration of 6×10^{-3} M, was then added to the suspension in order to charge the $CoFe_2O_4$ particles. The formed suspension was ultrasonicated for 10 minutes. X-ray diffraction measurements performed on the $CoFe_2O_4$ powder, before its dispersion on the suspension, indicated that it was composed by $CoFe_2O_4$ with the cubic spinnel structure.

In order to deposit the thin films, two parallel electrodes were placed inside the suspension, separated by a distance of 20mm. p-Si substrates were used for the cathode, while the anode was composed by Si/SiO2/TiO2/Pt (platinum covered silicon substrate). The dc voltage applied between the electrodes, during the electrophoresis process, was 24.5V. The deposition time was 130 min. After the electrophoresis preparation, the samples were heated at 50ºC during 1 hour to evaporate liquid residues and then annealed at 400ºC, 500ºC and 600ºC, during 2 hours.

The structural studies were performed by X-ray diffraction (XRD) and were carried out with a Philips PW-1710 diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) was performed with a Nova NanoSEM 200 microscope. The magnetic properties were measured with an Oxford Instruments vibrating sample magnetometer (VSM).

3. Results and discussion

Figure 1a) shows the X-Ray diffraction spectra measured on the as-deposited film (heated at 50ºC) as well as on the films annealed at 400ºC, 500ºC and 600ºC. The vertical solid lines indicate the bulk peak positions of $CoFe_2O_4$ with the cubic spinnel structure. The observed diffraction peaks were fitted with gaussian functions in order to determine their peak positions and peak widths. The diffraction spectra show that the films are polycrystalline and composed by cobalt ferrite with the cubic spinnel structure. The peak positions, are similar to the ones for bulk cobalt ferrite, corresponding to a lattice parameter of $a = 8.3874$ Å. The thickness of the films, determined from cross-section SEM micrographs, was ~250 nm.

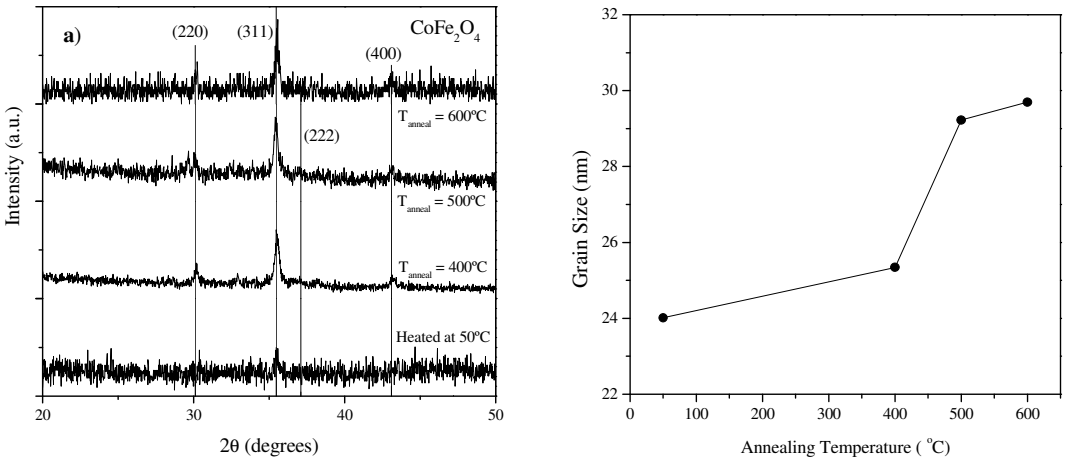

Figure 1: X-ray diffraction spectra of the cobalt ferrite films, for a) as-deposited and b-d) annealed at 400ºC, 500ºC and 600ºC. In b) is the grain size determined from the (311) diffraction peak of each sample.

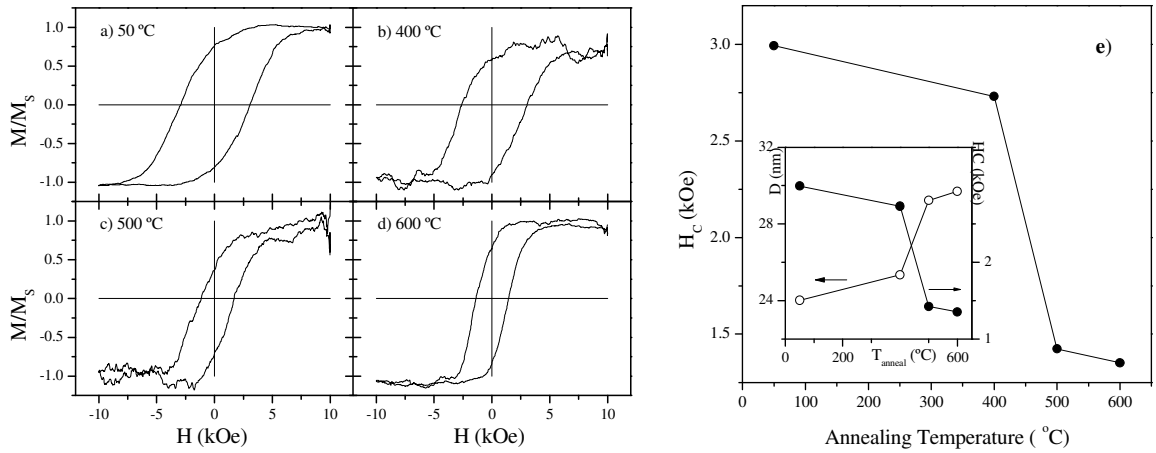

Figure 2: In a)-d) are the magnetization hysteresis cycles measured at room temperature on the heat-treated samples. In e) is the coercive field obtained from the loops. The inset shows a comparison of the grain size obtained from the X-ray diffraction spectra and the coercive field.

The grain sizes (D) of the ferrite films were determined from their corresponding (311) X-ray diffraction peak width, using the Scherrer equation [15]. Figure 1b) shows the obtained values as a function of the heat treatment temperature. The grain size of the prepared films grows from 24 nm, on the sample annealed at 50ºC, to 30 nm, for the one annealed at 600ºC, indicating the progressive agglomeration of the nanosized grains due to the heat treatment.

Figures 2a-2d) show the magnetization hysteresis loops, measured at room temperature, on the film heated at 50ºC and on the ones annealed at 400 ºC, 500ºC and 600ºC. The loops were obtained with the magnetic field applied on the plane of the films and were corrected by subtracting the diamagnetic contribution from the substrate. They were normalized relative to the saturation value of each sample. Figure 2e) shows the variation of the coercive field (H_C) as a function of the annealing temperature, determined from the measured hysteresis cycles. The coercive field of the samples decreases as the annealing temperature increases, due to the corresponding increase on the grain size, as observed from inset of figure 2e).

Owing to the magnetocrystalline anisotropy, Co-ferrite particles are magnetically monodomain for sizes smaller than 40 nm [16], such as in the case of the films here studied. Additionally, the films are composed by small nanosized grains (below 30 nm) and these monodomain ferrite particles are dispersed with random orientations on the polycrystalline films. For particles with cubic anisotropy the coercive field is $H_C=2K_1/M_S$ [17], where K_1 is the magnetocrystalline anisotropy constant and M_S is

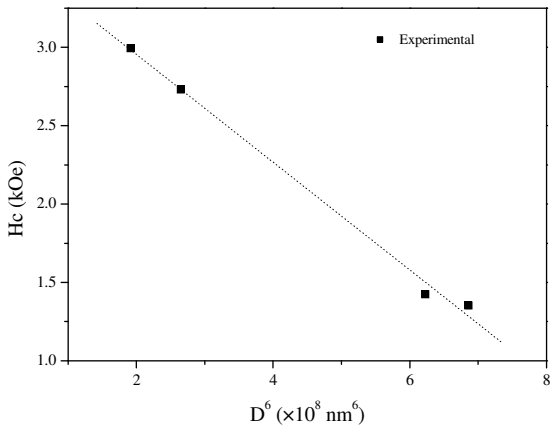

Figure 3: Coercive field as a function of the sixth power of the grain size of the films.

the saturation magnetization. In the absence of the exchange interaction between the magnetic moments of the particles each one would align independently with its own easy direction of magnetization. However, the exchange energy imposes parallel alignment of the moments on a length scale $L = \sqrt{A/K}$ [18], where A is the exchange stiffness. Thus, if L is larger than the anisotropy correlation length, as in nanosized particles [18,19], the alignment of the moments with the easy direction is hindered. Then, based on the random anisotropy model for nanocrystalline magnetic particles [18], an effective anisotropy constant appears $K = K_1/\sqrt{N}$ where N is the number of grains in the magnetically coupled volume: $N = (L/D)^3$. This then leads to an effective anisotropy of $K = K_1^4 A^{-3} D^6$. Since $H_C \propto K$, on this model the coercive field is then proportional to D^6 and for nanosized magnetic particles a fast variation of H_C with the grain size is predicted. Figure 3 shows the coercive field as a function of the sixth power of grain size for the different heat treated films The approximately linear behavior observed on the figure is then indicative that random anisotropy plays an important role on the magnetic properties of the nanosized grained electrophoretic deposited films.

4. Conclusions

Cobalt ferrite thin films have been deposited by electrophoresis on p-doped Si substrates. Their structural and magnetic properties have been characterized for different annealing temperatures. The films were polycrystalline and composed by $CoFe_2O_4$ with the cubic spinnel strucutue. Their grain sizes were small (below 30 nm) and increased with increasing annealing temperature. The observed decrease of the coercive field with grain size reflected the competition between the magnetocrystalline anisotropy and the exchange coupling energy on the the nanosized grained films.

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