Structural and magnetic properties of $CoFe_2O_4$ thin films deposited by laser ablation on Si(001) substrates

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Abstract: Cobalt ferrite ($CoFe_2O_4$) thin films have been deposited on Si(001) substrates, with different substrate temperatures (Tdep = 25ºC-600ºC). The films were prepared by pulsed laser ablation with a KrF excimer laser (wavelength λ=248nm). The oxygen pressure during deposition was 2×10^{-2} mbar. The films structure was studied by X-ray diffraction (XRD) and their surface was examined by scanning electron microscopy (SEM). The magnetic properties were measured with a vibrating sample magnetometer (VSM). For low deposition temperatures the films presented a mixture of a $CoFe_2O_4$ phase, with the cubic spinel structure, and cobalt and iron antiferromagnet oxides with CoO and FeO stoichiometries. As the deposition temperature increased the CoO and FeO relative content strongly decreased, so that for T_{dep} = 600ºC the films were composed mainly by polycrystalline $CoFe_2O_4$. The magnetic hysteresis cycles measured in the films were horizontally shifted due to an exchange coupling field (H_{exch}) originated by the presence of the antiferromagnetic phases. The exchange field decreased with increasing deposition temperature, and was accompanied by a corresponding increase of the coercivity and remanence ratio of the cycles. This behavior was due to the strong reduction of the CoO and FeO content, and to the corresponding dominance of the $CoFe_2O_4$ phase on the magnetic properties of the thin films.

Introduction

Cobalt ferrite ($CoFe_2O_4$) thin films are good candidates for applications in magneto-optical devices or high-density recording media [1-3], due to their high coercivity, high magnetocrystalline anisotropy and moderate saturation magnetization [4]. More recently, $CoFe_2O_4$ has also been used in magnetoelectric composite thin films [5,6], due to its high magnetostriction.

$CoFe_2O_4$ has an inverse spinel structure [7] in which the octahedral B sites are occupied by eight Co^{2+} and eight Fe^{3+} cations, while the tetrahedral A sites are occupied by the remaining eight Fe^{3+}. In thin film form its magnetic anisotropy strongly depends on the amount of strain. By selecting substrates with different lattice parameters, or depositing the films at different substrate temperatures, it is possible to change their preferred orientation, the amount of stress imposed and hence their magnetic properties [8]. Also, the presence of residual oxide phases, such as CoO and FeO, which are antiferromagnetic [7], affects the thin films magnetic properties.

In this work, we have deposited cobalt ferrite thin films at different substrate temperatures. The influence of the substrate temperature on the presence of residual phases and their connection with the structural and magnetic properties will be reported.

Experimental

The films were prepared by pulsed laser ablation on Si(001) substrates. The depositions were done using a KrF excimer laser (λ=248nm), at a fluence of 1.5J/cm^2. The pulse length of the laser was 25ns and the repetition rate was 10Hz. The target was composed by a compressed cobalt ferrite powder, sintered at 1100ºC during one hour. The X-ray diffraction spectrum measured on the target showed that it was polycrystalline and composed by $CoFe_2O_4$ with a cubic, spinel type, structure. Its lattice parameter obtained from the X-ray diffraction spectrum was a=8.393Å, which is close from the bulk one (a=8.3919Å [11]).

The thin films were deposited in a reactive O_2 atmosphere a pressure (pO_2) of 2×10^{-2} mbar and the substrate temperature varied from room temperature to 600ºC. The distance from the target to the substrate (d_{ST}) was 2.3cm. The structural studies were performed by X-ray diffraction (XRD) and were carried out with a Philips PW-1710 diffractometer using Cu Kα radiation. The surface of the films was examined by scanning electron microscopy (SEM). The magnetic measurements were performed at room temperature, with a vibrating sample magnetometer (VSM). The magnetic field was applied parallel to the films surface.

Results and discussion

Figure 1 shows SEM micrographs obtained on samples deposited with substrate temperatures a) T_{dep}=25ºC (room temperature) and b) T_{dep}=600ºC. Inherent to the laser ablation technique is the appearance of small droplets on the films surface, with sizes in the range ~0.5-2μm [10]. The films deposited at lower temperatures present a granular surface with an average grain size of 0.7μm, determined from the SEM micrographs. However, for higher substrate temperatures the surface presents grains with much smaller size and the surface is smother (as observed by SEM), presenting a low density of these droplets, as shown in figure 1b) for the particular case of T_{dep}=600ºC. The thickness of the films, determined from cross-section SEM micrographs, was ~100nm.

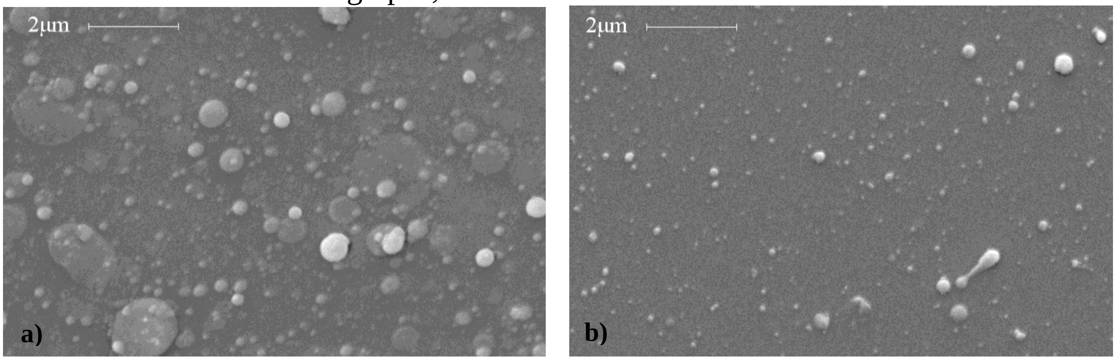

Figure 1 - SEM micrographs for films grown with $pO_2=2\times10^{-2}$mbar and substrate temperatures a) T_{dep}=25ºC and b) T_{dep}=600ºC.

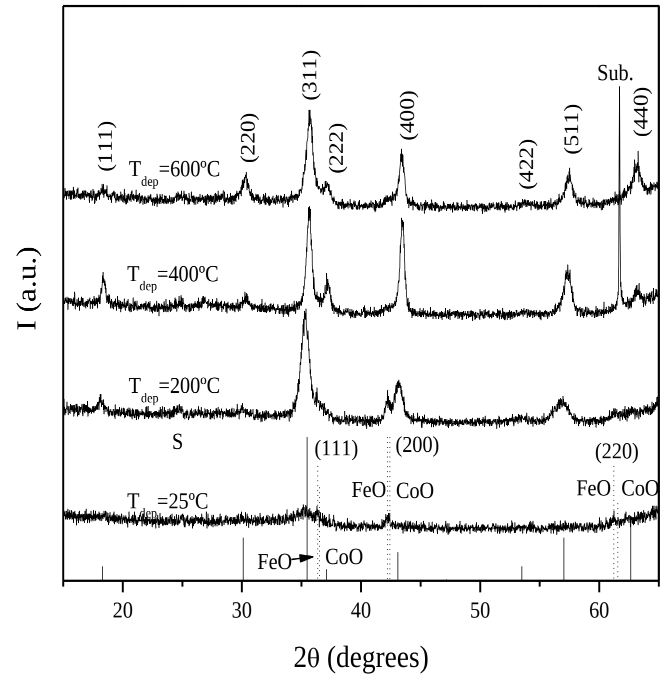

Figure 2 - X-ray diffraction spectra for films grown at substrate temperatures 25ºC, 200ºC, 400ºC and 600ºC. The vertical lines mark the peak positions of the bulk $CoFe_2O_4$ cubic spinel phase (—) and of the cubic CoO and FeO bulk phases (···).

Figure 2 shows the X-ray diffraction spectra measured on films deposited at room temperature (25ºC), 200ºC, 400ºC and 600ºC. The vertical solid lines indicate the peak positions of the bulk $CoFe_2O_4$ cubic spinel phase and the vertical doted lines indicate the peak position of the cubic CoO and FeO phases [9]. The diffraction patters show that the films are composed by a mixture of the $CoFe_2O_4$ spinel phase, and cobalt and iron oxides with CoO and FeO stoichiometries. For T_{dep}=600ºC the relative intensities of the peaks of $CoFe_2O_4$ are close to the bulk ones. However, at lower temperatures their relative intensity does not coincide with the corresponding ones for a bulk $CoFe_2O_4$ powder, indicating some degree of texturing. For deposition temperatures of 200ºC the intensity of the (311) peak is enhanced relative to the others indicating a (311) preferential orientation. For T_{dep}=400ºC the (400) peak is enhanced as compared to the other ones indicating a change in the preferential growth.

The proportion of the CoO and FeO phases, relative to the $CoFe_2O_4$ one, vary with substrate temperate. Figure 3 shows the relative intensity between the (200) peak of the cubic CoO and FeO phases and the (311) peak of the cubic spinel $CoFe_2O_4$. For low substrate temperature the relative intensity is near 1, indicating that the amount of these phases is similar to the $CoFe_2O_4$ one. However, by increasing the substrate temperature the relative intensity strongly decreases to a value near 0.07 at T_{dep}=600ºC, so that mainly the $CoFe_2O_4$ phase composes the films. Nevertheless, a residual amount of the CoO and FeO phases still remain in the films deposited at 600ºC.

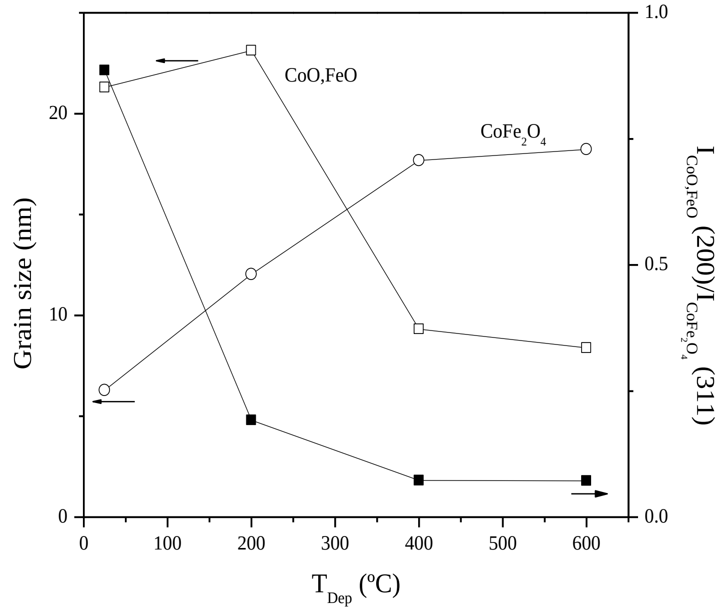

Figure 3 - Relative intensity between the (200) peak of the cubic CoO and FeO phases and the (311) peak of the cubic spinel $CoFe_2O_4$. The grain sizes of the $CoFe_2O_4$ and CoO-FeO phases are also shown.

The grain sizes of the $CoFe_2O_4$ and CoO-FeO phases, were determined from the $CoFe_2O_4$-(311) and (CoO,FeO)-(200) peak widths, by using the Scherrer equation [11]. They are also shown in figure 3. The reduction of the CoO and FeO content is accompanied by a overall reduction of their grain sizes, from 21.3nm at T_{dep}=25ºC to 8.4nm at T_{dep}=600ºC, and to an increase of the grain size of the $CoFe_2O_4$ phase from 6.3nm at T_{dep}=25ºC to 18.2nm at T_{dep}=600ºC. At room temperature the films are more disordered because during growth there was not enough thermal energy for the atoms to migrate in the surface which hinders the coalescence in bigger CoO and FeO grains. At higher temperature the low content on CoO and FeO also inhibits the presence of bigger grains. At 200ºC, in spite of the decrease of the content of CoO and FeO, the thermal energy is sufficient to allow coalescence in bigger grains giving a small maximum at this temperature.

The variation of the lattice parameter of the $CoFe_2O_4$ phase, with deposition temperature, is shown in figure 4. The lattice parameter decreases with increasing annealing temperature, but for temperatures lower than 400ºC the lattice parameter is expanded relative to the bulk ferrite whereas for temperatures $T_{dep} \geq 400$ºC it is contracted. A similar behavior has also been observed on thin films deposited on MgO (100) substrates [12].

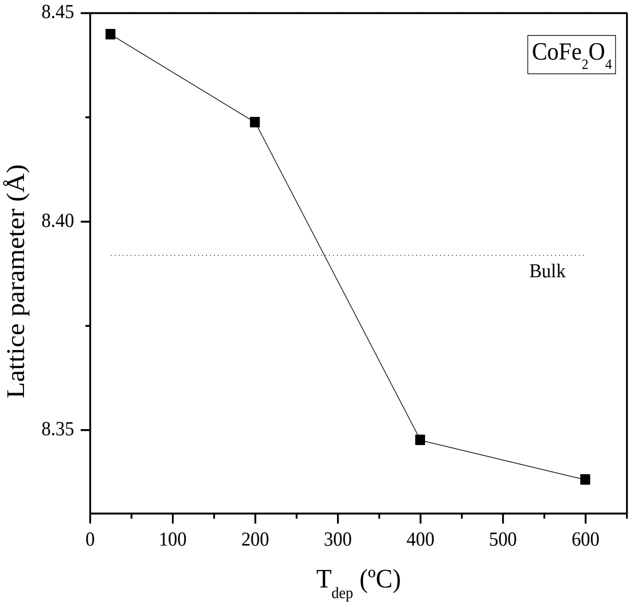

Figure 4 - Lattice parameters observed for films grown at substrate temperatures 25ºC, 200ºC, 400ºC and 600ºC.

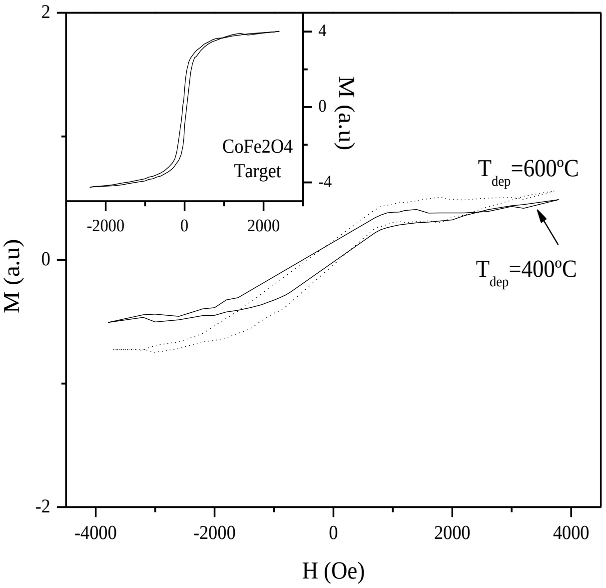

Figure 5 - Hysteresis loops measured at room temperature on the samples deposited at substrate temperatures 400ºC and 600ºC. The inset shows the corresponding hysteresis loop of the ablated $CoFe_2O_4$ target.

Figure 5 shows the magnetization measured on the samples deposited at 400ºC and 600ºC. For comparison, the magnetization measured on the ablated target is shown in the inset of the figure. The films loops are slightly horizontally shifted indicating the presence of an exchange coupling field between the $CoFe_2O_4$ and another magnetic phase. Since CoO and FeO are antiferromagnetic [13] with Néel temperatures of 291K and 200K,

Table 1 – Coercive fields (H_c) and remanence ratios (M_{sat}/M_{rem}), obtained from the magnetization loops measured at room temperature. T_{dep} indicates the substrate temperature during film deposition.

T_{dep} (ºC)	H_c (Oe)	M_{sat}/M_{rem}
25	230	0.16834
400	306	0.18851
600	432	0.24572

respectively, while the measurements were made at 298K, this is mainly due to the CoO phase. The exchange coupling field is 235Oe for the film deposited at 400ºC and 170Oe for the film deposited at 600ºC. The decrease of the exchange field is due to the lowering of the content of the antiferromagnetic phases with increasing deposition temperature.

Table 1 summarizes the coercivity, remanence ratio and saturation magnetization for the films deposited with T_{dep}=25ºC, 400ºC and 600ºC. The coercivities and remanence ratios of the thin films are somewhat lower than the bulk value of ~900Oe, but increase with increasing deposition temperatures. This is a consequence of the reduction of the amount of CoO and FeO phases, which reduces their antiferromagnetic contribution to the hysteresis loops, with a corresponding dominance of the magnetic contribution of the $CoFe_2O_4$ phase. Thus, increasing the deposition temperature hinders the formation of the residual phases and inhibits their contribution to the magnetic properties of the cobalt ferrite thin films.

Conclusions

$CoFe_2O_4$ thin films have been deposited by laser ablation on Si(001) substrates, at different substrate temperatures. The films presented a mixture of a $CoFe_2O_4$ cubic spinel phase, with antiferromagnetic CoO and FeO with cubic structure. As the deposition temperature increased the CoO and FeO relative content strongly decreased, so that for T_{dep} = 600ºC only a residual amount was observed. The presence of CoO and FeO caused a shift of the magnetic hysteresis cycles and a reduction of their coercivity and remanence ratio as compared to the bulk $CoFe_2O_4$. Thus, when preparing cobalt spinel ferrite thin films particular attention must be paid to the presence of these residual phases as they hinder their magnetic properties. However, increasing the deposition temperature can reduce their content in the films.

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