Cobalt Ferrite Films: Nanopolishing and Magnetic Properties

Vitaliy Bilovol[1], Laura G. Pampillo[1], Dagmar Meier[2], Ulrike Wolff[2], and Fabio Saccone[1]

[1]Laboratorio de Sólidos Amorfos, INTECIN-CONICET, Facultad de Ingeniería, Universidad de Buenos Aires, Buenos Aires C1063, Argentina
[2]Leibniz-Institut für Festkörper-und Werkstoffforschung Dresden, Dresden 01069, Germany

$CoFe_2O_4$ films were deposited on Si [(100) or (111)] substrates by pulsed laser deposition, varying substrate temperature and deposition time. All films showed highly (111)-preferred orientation. Magnetic measurements (hysteresis loops) at room temperature indicated that the films have in-plane magnetic anisotropy. By atomic force microscopy, the surface topology revealed an average roughness of approximately 15 nm due to the presence of droplets. To define the relevance of droplets on the films' magnetic properties, we applied a nanopolishing technique after which the surfaces became notoriously smoother. As a consequence of this surface modification, we found that the hysteresis loops (measured again after nanopolishing) revealed changes in the magnetic response of the samples. The thinner films ($t \approx 50$ nm) revealed waist-type hysteresis loops with diminished values of the coercive field, while the thickest film ($t \approx 100$ nm) increased its coercive field without qualitative change in its loop shape. We attributed the altered magnetic response to different mechanisms that depend on sample thickness. For the thinner films, an additional anisotropy (to that existing in the plane) was induced after the nanopolishing procedure. For the thickest film, it was observed that differences are present after the elimination of the droplets, showing their important role in the magnetic response of the films.

***Index Terms*— $CoFe_2O_4$ films, droplet, nanopolishing.**

I. INTRODUCTION

PULSED laser deposition (PLD) has been developed to be a standard technique for the growth of thin films. Under certain PLD conditions, the appearance of droplets onto the film surface is very common. Their presence can be highly undesirable in certain applications, especially in cases of thin magnetic films where the droplet contribution to the global magnetic response could be significant.

In the literature, there are few reports on studies of superficial droplets [1], [2], but nothing was mentioned about their influence on the magnetic properties of thin films.

In this paper, by means of magnetic measurements and atomic force microscopy (AFM), we investigated the role of superficial droplets on the magnetic properties of cobalt ferrite films. Therefore, we measured hysteresis loops before and after applying the nanopolishing technique [3]. By this way, we followed the magnetic behavior of the films and observed that it is qualitatively altered after the polishing procedure.

II. EXPERIMENT

The films of $CoFe_2O_4$ were deposited on Si (111) or Si (100) substrates by PLD using an Nd:YAG (yttrium-aluminum-garnet) laser at a wavelength of 355 nm and a repetition rate of 10 Hz. A fixed laser power of 0.55 W was used, with a mean fluence of 2.0 J/cm^2. The pressure in the chamber during the deposition was 0.04 mbar at different substrate temperatures (500 °C, 600 °C, and 700 °C). Deposition time was 10/20 min with an average deposition rate of about 5 nm/min. Thin films of spinel ferrites were prepared using 1.5 cm diameter and 3 mm thick disk target synthesized by sol-gel techniques. The details of sample synthesis and their corresponding labels are summarized in Table I. Structural properties were analyzed by X-ray diffraction (XRD) in a $\theta - 2\theta$ diffractometer (Rigaku D/max equipped with a vertical goniometer) using Cu–Kα radiation.

The nanopolishing was performed on the Logitech PP5D Precision Polishing Jig, which is known for its fine polishing quality. The samples were glued onto a glass plate using quartz wax (Ocon 200, Logitech), and were vacuum mounted on the polishing head. The polishing machine PM5 from Logitech allows a variation of the rotating speed from 0 to 70 rotations/min with a loading weight from 0 to 2800 g. The polishing pressure can be set according to the size and structure of the samples.

For polishing of our films, the parameters were selected as follows: 200 g loading weight and 20 r/min for 10 min. As the films are sensitive to water, a polishing solution (OP-AN neutral alumina suspension, Struers, pH 7–7.5, 0.02 μm) dissolved in red lubricant (0.05 g in 50 mL, Buehler) was used. After polishing, the films were cleaned for 5 min using the same polishing procedure but with a clean polishing towel and pure red lubricant as a cleaning solution.

The surface morphology of the samples was imaged with a DI 3100 AFM in tapping mode. The AFM tip was a commercial Si tip (Rotated Tapping Etched Silicon Probe, Veeco). The magnetic properties were investigated in a quantum design Physical Property Measurement System vibrating sample magnetometer. Room-temperature near edge X-ray-absorption fine structure (XANES) spectra at the Fe K-edge was recorded in fluorescence mode using an Si(111) monochromator in the beamline of the Laboratório Nacional de Luz Síncrotron (LNLS) (Campinas, Brazil).

III. RESULTS AND DISCUSSION

The diffractograms of all samples are shown in Fig. 1. (111)-preferred orientation for cobalt ferrite films with a low intensity of the (311) reflection is observed when deposited

Manuscript received June 14, 2013; revised September 4, 2013 and January 9, 2014; accepted April 3, 2014. Date of publication April 11, 2014; date of current version September 9, 2014. Corresponding author: V. Bilovol (e-mail: vbilovol@fi.uba.ar).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/TMAG.2014.2316481

TABLE I

FILM DEPOSITION CONDITIONS AND MAIN CALCULATED PARAMETERS OF THE FILMS: T_{dep}—DEPOSITION TEMPERATURE, t—DEPOSITION TIME, H_{c}—COERCIVE FIELD, S—SQUARENESS, $d_{(222)}$—INTERPLANAR DISTANCE, AND R_{rms}—ROUGHNESS

sample	T_{dep} (°C)	t (min)	Si	H_c (Oe) in-plane	S (M_r/M_s)	$d_{(222)}$ (Å)	R_{rms} (nm)
S1	500	10	(100)	1850	0.46	2.4248	15.9
S2	600	10	(100)	2085	0.54	2.4171	25.4
S3	700	10	(100)	1085	0.44	2.4135	18.5
S4	600	10	(111)	885	0.36	2.4177	13.3
S5	600	20	(100)	445	0.30	2.4028	11.7

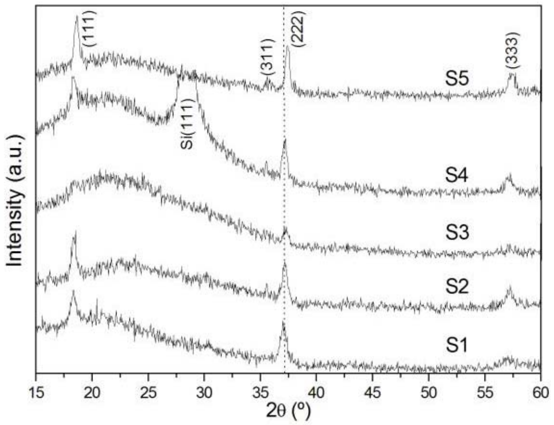

Fig. 1. Diffractograms of all samples (as prepared).

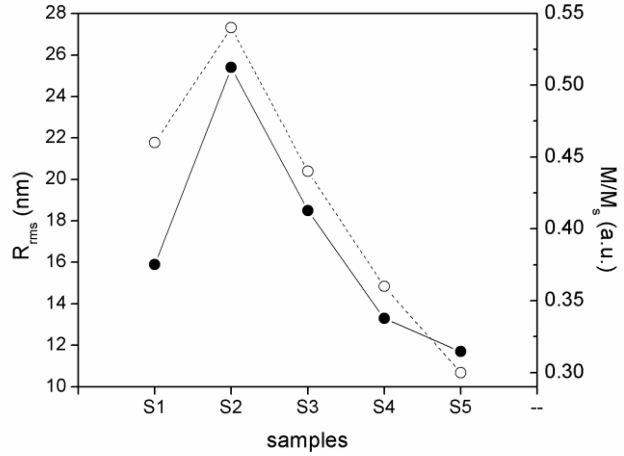

Fig. 2. R_{rms} values (dark circle) and $M_{\mathrm{r}}/M_{\mathrm{s}}$ ratios (open circle) for all samples (before nanopolishing). The lines are set only as a guide for the eye.

both on Si (100) and Si (111) substrates. Similar results were obtained in [4]. Considering the (222) peak of the spinel, we calculated the interplanar spacing $d_{(222)}$, which decreases with the increase of the substrate temperature during deposition. A similar tendency was observed in [5]. This indicates that cobalt ferrite films have in-plane tensile residual strain due to a thermal mismatch between cobalt ferrite and silicon. Due to this mismatch, an in-plane isotropic tension will be induced in cobalt ferrite films during cooling from deposition time to room temperature [6]. In addition, a decrease of the $d_{(222)}$ for the sample deposited at the same temperature with twice the thickness was observed. Although it is expected that the residual strain should be released by increasing the thickness. A similar tendency was reported in [7]. Besides, with the selected orientation of the Si substrate, (111) or (100), we found that the interplanar spacing stays almost unchanged for the same temperature and deposition length, indicating that the orientation of the silicon substrate does not affect the dimension of the cobalt ferrite lattice. The calculated interplanar distances are shown in Table I.

AFM imaging showed the existence of droplets on the film surfaces. This fact can explain the rather high value of the surface roughness. A higher R_{rms} was observed when the substrate temperature increases from 500 °C to 600 °C (Table I). Our results are in accordance with [7], which used PLD technique and similar and fluency observed lower R_{rms} values for thicker ferrite cobalt films. In our case, we found that the roughness of the films is lower (at $T = 600$ °C) when the thickness is doubled (comparing S2 with S5).

When the magnetization of the films was measured as a function of the applied magnetic field, unambiguous features were noted for all films. As in the case of the films reported in [8], our films are highly in-plane anisotropic. This becomes clear from the in-plane and out-of-plane magnetic measurements (see the following). In accordance with [6], the main contributions to the energy of cobalt ferrite films are magnetocrystalline, shape, and stress anisotropy.

For sample S5, equal coercive fields for the in- and out-of-plane hysteresis loops were observed. On the contrary, for the thinner samples, this effect was not observed. This is due to the increasing film thickness promoting that shape anisotropy lost its relevance. The characteristic values of the hysteresis loops are gathered in Table I.

Plotting the squareness ($M_{\mathrm{r}}/M_{\mathrm{s}}$) and R_{rms} values for all samples studied in this paper, we noticed that both magnitudes follow the same tendency (Fig. 2). For instance, sample S2 revealed maximum values, while sample S5 showed minimum ones. This indicates that there is a direct relationship between the surface topology and the magnetic properties of the films. To investigate this fact, we decided to apply the nanopolishing technique (for more details about the technique, see [3]) to remove the droplets from the films' surfaces. If the droplets play a significant role in the magnetic response, after their removing, the magnetic response of the films should be altered not only quantitatively but qualitatively as well.

After the nanopolishing procedure, AFM imaging was applied again. The analysis of new measurements revealed that the R_{rms} value was considerably reduced ($R_{\mathrm{rms}} < 4$ nm) in all samples (Figs. 3 and 4).

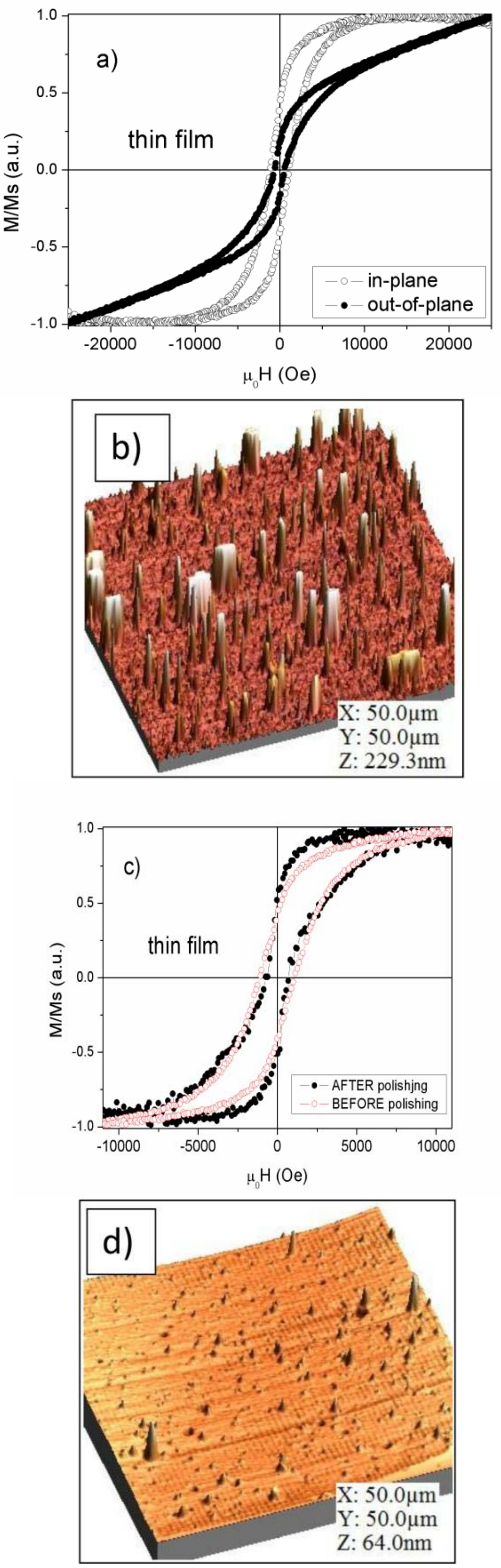

Fig. 3. (a) Hysteresis loops before nanopolishing of S2 (in-plane and out-of-plane). (b) Corresponding AFM image. (c) Comparison of the hysteresis loops (in-plane) before and after nanopolishing. (d) AFM image after nanopolishing.

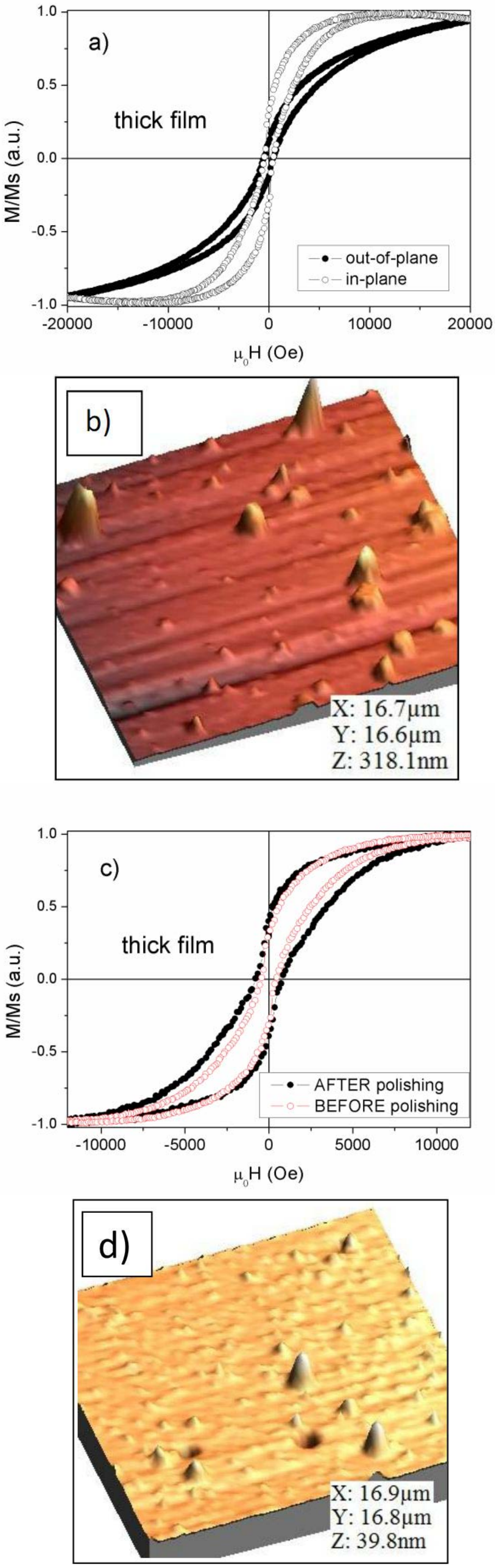

Fig. 4. (a) Hysteresis loops before nanopolishing of S5 (in-plane and out-of-plane). (b) Corresponding AFM image. (c) Comparison of the hysteresis loops (in-plane) before and after nanopolishing. (d) AFM image after nanopolishing.

From the hysteresis loops, we can distinguish two types of magnetic behavior. For all samples deposited for 10 min, the hysteresis loop became waist type with notable decrease in the value of coercive field. On the contrary, the sample deposited for 20 min showed an augmented coercive field after the polishing, preserving the shape of the loop.

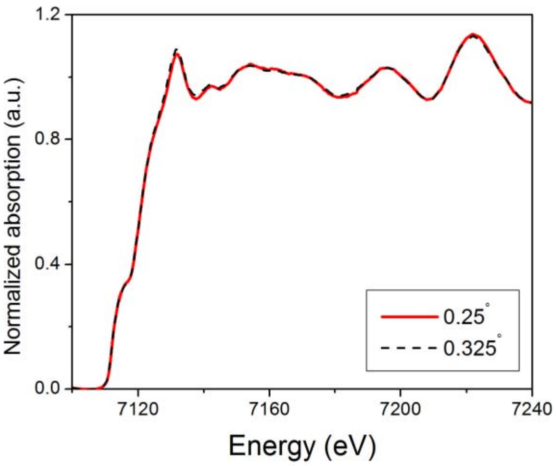

Fig. 5. XANES signals of S5 sample (before polishing) measured at Fe K-edge in grazing incidence geometry (0.25° and 0.325°).

In Figs. 3 and 4, respectively, we show the hysteresis loops of S2 and S5 samples where the only difference is in the time of deposition.

This gives us an intuitive explanation of a new magnetic behavior the samples have after nanopolishing. Following the description of [9], we can consider the thicker sample S5 as consisting of two magnetic parts: 1) the film with high thickness and high coercive field (magnetically hard) and 2) magnetically soft droplets. Therefore, the contributions of both parts of such phases generally give, as it is well known, a waist-type hysteresis loop. The increase of the coercive field of this film after polishing is due to removing part of the droplets situated on the sample surface: the relative weight of the magnetically soft part of the sample was reduced, while the contribution of the magnetically hard film became more important and the coercive field naturally increased at the expense of the prevailing magnetically soft phase.

To sustain the hypothesis of soft and hard phase, we measured XANES profiles in GIXAS geometry of S5 film (before polishing) at Fe K-edge using two incident angles: 1) 0.25° and 2) 0.325°. By this, we sensed Fe environment of less and more deep layers of the sample, respectively. As it can be observed from Fig. 5, XANES profiles are identical meaning that Fe environment is similar in less and more deep layers of the system, suggesting sample homogeneity in chemical composition.

Apparently, other magnetic phenomena are presented in the thinner films. We observed a qualitatively altered magnetic behavior when it is compared with the one before nanopolishing. We can highlight two differences in the loop attributes. The first one is the decrease of the coercive field. This behavior is known to be expected for thinner films [9]. Then, we may suppose that a part of the surface was removed after nanopolishing together with droplets, but this scenario seems to be not our case as it can be seen from AFM images (Fig. 3); even after the polishing procedure had been applied, some droplets were not completely removed only reduced in height. The second feature is the waist-shaped hysteresis loop. This could be related to deformation of the thin film after mechanical contact with the polishing device. It should be noticed that during nanopolishing, the samples were submitted to a 20 kPa pressure that could induce stress and deformation in the thin films (about 50 nm). The constricted hysteresis loops suggest that the polishing induced additional in-plane anisotropy (stress-induced anisotropy) along the plane of polishing. Similar effects are reported for other systems as Mn–Fe or Zn–Fe ferrite single crystals [10]. Moreover, as it can be seen from Fig. 3 for thin cobalt ferrite films before and after polishing, the magnetization curve after polishing saturates at lower applied field. This way, the in-plane magnetic anisotropy was only reinforced after polishing (due to the induced stress). Such a behavior is not observed in the thick film (Fig. 4) because either the additional in-plane anisotropy was not induced in this film or it is not significant.

Finally, to corroborate the hypothesis about possible deformation of the films as a result of polishing, we inspected the region of (222)-Bragg peak by XRD measurements of two polished films: 1) the thinner (S2) and 2) the thicker one (S5). In both cases, the effect of nanopolishing was to increase the interplanar distance, $d_{(222)}$. This indicates that the plane perpendicular to the surface elongated after nanopolishing has been applied. However, the effect was notoriously different for each film. Meanwhile, in the thick film, the elongation was barely distinguishable (near 0.11% as compared with nonpolished S5 film), the thin film revealed more notorious change (about 0.66% as compared with nonpolished S2 film). These results agree very well with our assumptions made before.

IV. CONCLUSION

A series of cobalt ferrite films was prepared by PLD varying the deposition temperature, substrate texture, and deposition time. In all films, (111)- preferred crystallographic orientation of $CoFe_2O_4$ was detected. Clear in-plane magnetic anisotropy was observed for all explored films. AFM measurements revealed a considerable value of roughness due to droplets on the film surfaces. Applying a nanopolishing technique to the films, qualitatively new tendencies in their magnetic responses were observed depending on the film thickness. The thick film's magnetic behavior is consistent with the previous work on $CoFe_2O_4$ films and the model proposed by Rigato *et al.* [9], which describe the anisotropy of the entire film as composed of partial contribution from an in-plane anisotropy fraction (at deeper layers) and a softer region (at surface). Removal of droplets from the surface of thick films induces a certain hardening of the film. On the other hand, for a thinner film, we found that besides the contribution of droplets to the global magnetic response, their sensitivity to mechanical stress due to the applied pressure during nanopolishing is higher.

ACKNOWLEDGMENT

This work was supported in part by the MINCyT-IFW Leibniz Project under Grant IF/10/01 and in part by LNLS, Campinas—SP, Brazil. The authors would like to thank S. Pofahl for the help with the atomic force microscopy measurements and nano-polishing.

REFERENCES

[1] T. Schmauder, A. Waldauf, H. Wald, and P. Seidel, "Influence of target-substrate angle on properties of laser deposited $YBa_2Cu_3O_{7-\delta}$ thin films and step-edge Josephson junctions," *Phys. C*, vol. 333, no. 1, pp. 23–30, 2000.

[2] A. Lorusso, V. Fasano, A. Perrone, and K. Lovchinov, "Y thin films grown by pulsed laser ablation," *J. Vac. Sci. Technol. A*, vol. 29, no. 3, p. 031502, 2011.

[3] T. Shapoval *et al.*, "Nanoscale wedge polishing of superconducting thin films—An easy way to obtain depth dependent information by surface analysis techniques," *Supercond. Sci. Technol.*, vol. 21, no. 10, p. 105015, 2008.

[4] J.-P. Zhou, H.-C. He, and C.-W. Nan, "Effects of substrate temperature and oxygen pressure on the magnetic properties and structures of $CoFe_2O_4$ thin films prepared by pulsed-laser deposition," *Appl. Surf. Sci.*, vol. 253, no. 18, pp. 7456–7460, 2007.

[5] C. Araujo, B. G. Almeida, M. Aguiar, and J. A. Mendes, "Structural and magnetic properties of $CoFe_2O_4$ thin films deposited by laser ablation on Si (001) substrates," *Vacuum*, vol. 82, no. 12, pp. 1437–1440, 2008.

[6] M. Khodaei *et al.*, "Strong in-plane magnetic anisotropy in (111)-oriented $CoFe_2O_4$ thin films," *J. Magn. Magn. Mater.*, vol. 340, pp. 16–22, Aug. 2013.

[7] D. Mukherjee, T. Dhakal, M.-H. Phan, H. Srikanth, P. Mukherjee, and S. Witanachchi, "Role of crystal orientation on the magnetic properties of $CoFe_2O_4$ thin films grown on Si (100) and Al_2O_3 (0001) substrates using pulsed laser deposition," *Phys. B, Condensed Matter*, vol. 406, no. 13, pp. 2663–2668, 2011.

[8] P. D. Thang, G. Rijnders, and D. H. A. Blank, "Stress-induced magnetic anisotropy of $CoFe_2O_4$ thin films using pulsed laser deposition," *J. Magn. Magn. Mater.*, vol. 310, no. 2, pp. 2621–2623, 2007.

[9] F. Rigato, J. Geshev, V. Skumryev, and J. Fontcuberta, "The magnetization of epitaxial nanometric $CoFe_2O_4$ (001) layers," *J. Appl. Phys.*, vol. 106, no. 11, p. 113924, 2009.

[10] K. Aso, "Mechanically induced anisotropy and its effect on magnetic permeability in single crystal ferrites," *IEEE Trans. Magn.*, vol. 14, no. 2, pp. 76–81, Mar. 1978.