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Magnetic properties of nanostructured $Co_xFe_{3-x}O_4$ ($0<x<0.2$) thin films obtained by a low-temperature soft solution processing method

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Abstract

Single phase, highly crystalline and uniform cobalt ferrite thin films were deposited on glass and silicon substrates in aqueous solutions at 80 °C through the liquid phase deposition (LPD) method. Regardless of the chemical composition, the $Co_xFe_{2-x}O_4$ ($0<x<1$) thin films identified with a crystal structure as spinel-type are homogeneous, being constructed by spherical particles. The magnetic films present a hysteretic behavior at room temperature with saturation magnetization values close to the bulk material and coercivities depending on the cobalt content.

Keywords: Semiconductors; Magnetic films and multilayers; Chemical synthesis; X-ray diffraction; Magnetic measurements

1. Introduction

With the miniaturization of electronic components, the development of new synthetic strategies for the selective deposition of transition metal ferrites MFe_2O_4 films is critical for the future of microelectronic circuitry. Consequently, a myriad of synthetic strategies, both physical and chemical which differ in the manufacturability, cost, complexity and environmental hazard have been developed in the last decade [1–5]. In the past few years Nagayama and coworkers proposed new synthetic approach for the deposition of dielectric films, called the liquid-phase deposition (LPD) [6]. This method consists of the direct precipitation of homogenous metal oxide films via the controlled hydrolysis of the corresponding solutions of transition metal-fluoro complexes in presence of a F^- scavenger:

$$MF^{(n-2m)-} + mH_2O \rightleftharpoons MO_m + nF^- + 2mH^+ \qquad (1)$$

Boric acid is suitable as fluoride scavengers by virtue of its ability to form a water-soluble, stable complex which will cause the shift of the equilibrium reaction towards formation of the metal oxide:

$$H_3BO_3 + 4HF \rightleftharpoons BF_4{}^- + H_3O^+ + 2H_2O \qquad (2)$$

While the liquid phase deposition method has been extensively used to prepare simple binary transition metal oxides, considerably less is known about the mechanism of formation of single-phase multi-component oxide films. Accordingly, there are only few reports on the synthesis of polycrystalline perovskite-type ABO_3 (A = Sr, Ba) thin films with a columnar morphology [7–9], as well as the formation of iron–nickel binary oxide films [10]. Recently, this method was extended by our group to the preparation of superparamangetic zinc ferrite films with a columnar morphology [11]. $CoFe_2O_4$ is a very promising material for the design of the next generation magnetic recording media by virtue of its high chemical stability, moderate magnetization and high coercivity. Therefore, the present investigation is focused not only to extend the liquid-phase deposition to the deposition of $CoFe_2O_4$ thin films adjustable chemical composition, but also to the study of their structural and magnetic properties.

2. Experimental

Film deposition was performed in open atmosphere using a magnetic hotplate and an external temperature controller. Source chemicals were reagent grade purity and used as received from Alfa Aesar. Prior to deposition, the substrates were degreased by washing repeatedly with acetone and then sonicated in MilliQ water. The parent solution was obtained by dissolving 0.3 g of FeO(OH) in a 1 M $NH_4F{\cdot}HF$ aqueous solution. FeOOH was precipitated from an aqueous solution of $Fe(NO_3)_3{\cdot}7H_2O$ upon addition of a diluted solution of ammonia. Then, a separate aqueous solution of Co^{2+} with a concentration of 2 M was prepared by dissolving the corresponding amount of cobalt nitrate $Co(NO_3)_2{\cdot}6H_2O$ in distilled water. Cobalt ferrite thin films were deposited on

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non-alkali glass plates (Corning no. 7059) substrates and p-type {1 1 1} single-crystal Si wafers, respectively. Three separate solutions of iron oxyhydroxide, $Co(NO_3)_2$ and boric acid (aqueous solution $c = 0.5$ M) were mixed in different proportions to obtain a final solution with fixed concentrations of iron and H_3BO_3, respectively. Thus, the concentration of the Co^{2+} was varied in the range 0.1–0.5 M. Substrates were suspended vertically and soaked in the reaction solution at 80 °C for different periods of time, typically ranging between 20 and 120 min. To ensure complete crystallization of the resulted cobalt ferrite films, samples were subjected to a heat treatment in open air at 500 °C followed by a natural cooling to room atmosphere. Surface morphology and microstructure of the films was studied by using a JEOL-JSM 5410 scanning electron microscope, whereas their thicknesses were measured by a surface profile measuring system Dektak-IIA. Identification of the crystalline phases, crystallite size and the phase purity of the films were examined by X-ray diffraction using a Philips X'Pert System equipped with a curved graphite single-crystal monochromator (Cu Kα radiation).

The metal contents of the deposited zinc ferrite films were determined by inductive coupled plasma (ICP) spectroscopy, using a Varian FT220s flame absorption spectrometer.

3. Results and discussion

A low-temperature, single-step deposition of solutions of transition metal salts in $NH_4F{\cdot}HF$ leads to uniform, scratch resistant, well adherent cobalt ferrite films with thickness which can be easily controlled by varying the deposition time. As we demonstrated elsewhere, the slow hydrolysis of transition metal oxy-fluoro-anions first leads to supersaturated solutions of oxides/hydroxides which further precipitate onto the substrate to produce a high quality film [11]. For a given deposition time, the increase of the reaction temperature accelerates the film deposition which, in turn will result in a thicker film. The film thickness was found to vary roughly linearly with the deposition time and ranges typically between 50 and 400 nm for a deposition time of 20–180 min. Additionally, the Co/Fe ratio of the deposited films was found to follow closely the Co/Fe ratio of the treatment solutions, which clearly shows that the composition of the film can be strictly controlled by varying the transition metal concentration in the reaction solution. The X-ray diffraction patterns of the as-deposited $Co_{0.05}Fe_{3.95}O_4$ film (Fig. 1(a)) exhibits peaks which can be indexed as crystalline FeO(OH). Because the peaks attributable to the cobalt intermediates are not discernible in the respective patterns, but cobalt was identified by both the EDX and ICP measurements, we conclude that the respective Co(II) oxides/hydroxydes forming during the deposition are amorphous in nature and are therefore, not detectable by X-ray diffraction. Interestingly, the ICP measurements did not identify detectable traces of fluorine, which indicates that, although the synthetic approach involves a metal-fluoro complex as the reaction precursor, after the heat treatment at 600 °C, the resulting films are free of fluorine. Fig. 1(b) shows the X-ray diffraction patterns of ∼200 nm $Co_xFe_{3-x}O_4$ as-prepared and annealed films with, with x varying between 0.05 and 0.20. Samples consist of a single, well-crystallized phase with well-defined diffraction peaks which appear in addition to the broad pattern originating from the glass substrate. In depth analysis of the XRD patterns also shows that the XRD peaks slightly shift to higher angles upon increasing of the Co content of the films, which agrees well with a lowering of the cell parameter upon the replacement of the Fe^{2+} ions ($r_{Fe^{2+}} = 0.63$ Å) with the smaller Co^{2+} ions ($r_{Co^{2+}} = 0.58$ Å) [12].

However, for $x = 0.05$ and 0.15, a small reflection is observed at ≈33° in 2θ and can be ascribed to a α-Fe_2O_3 secondary phase. The small α-Fe_2O_3 impurity is presumably associated to the presence of a slight excess of iron in the corresponding treatment solutions and further confirms that the liquid-phase deposition method allows the fine tuning of the chemical composition of the ferrite films via a rigorous control of the metal ratio in the treatment solutions. For the film with the chemical composition of $Co_{0.1}Fe_{2.9}O_4$, the XRD peaks were indexed into a spinel-type cubic lattice with a refined cell parameter of $a = 8.38(4)$ Å, value which is in a good agreement with that reported for the bulk $CoFe_2O_4$ material ($a = 8.392$ Å) [13]. The crystallite size of the film was further determined from the modified Scherrer's formula [14], and found to be close to 20 nm. Fig. 2 illustrates a typical top-down SEM micrograph of the films corresponding to a ∼400 nm thick $Co_{0.2}Fe_{2.8}O_4$ film. Regardless of the chemical composition, all Co-ferrite films are uniform and constructed by spherical particles with a diameter of ∼250 nm.

Although the film's morphology does not vary noticeably upon annealing, some cracks can be detected in the case of the annealed films. These cracks were assumed to appear as a consequence of the differences between the thermal expansion coefficients of the ferrite and the glass substrate and can be

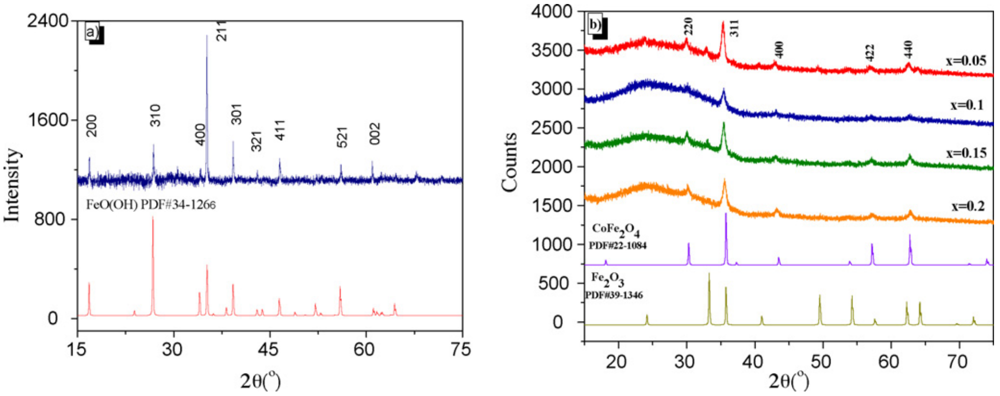

Fig. 1. X-ray diffraction patterns of the as-deposited $Co_{0.05}Fe_{2.95}O_4$ film (a) and ∼200 nm $Co_xFe_{3-x}O_4$ ($x = 0.05$–0.2) (b) annealed at 600 °C for 3 h. The simulated XRD patterns of $CoFe_2O_4$ and α-Fe_2O_3 are also represented for reference.

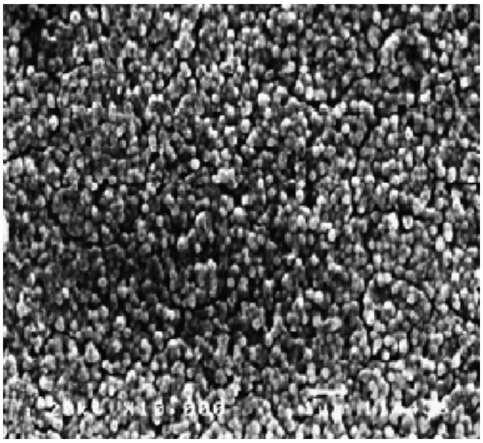

Fig. 2. Top-down SEM micrographs of a 200 nm $Co_{0.2}Fe_{2.8}O_4$ film deposited onto a Corning glass after heat treatment at 600 °C.

Table 1
Magnetic characteristics of $Co_xFe_{3-x}O_4$ films ($0 < x < 0.2$)

	a(Å)			
	8.40(80) ($x = 0.05$)	8.39(1) ($x = 0.1$)	8.38(4) ($x = 0.15$)	8.36(3) ($x = 0.2$)
$H_{c\ plane} \approx H_{c\perp}$ ($A\ m^{-1}$)	3.07	2.85	2.79	2.56
$SQ_{plane} \approx SQ_{\perp}$	0.65	0.61	0.64	0.65
M_s ($A\ m^2/kg$)[a]	78.8	76.1	67.9	68.1

[a] Determined by extrapolation of the high field values of the magnetization (from the linear dependency $M = f(1/H)$).

eliminated upon a slower cooling of the annealed films. The magnetic properties of the cobalt ferrite films were measured at room temperatures with a vibrating sample magnetometer Lakeshore 7307 by applying a magnetic field parallel and perpendicular to the film plane. A characteristic feature common to all the chemical compositions, is given by the hysteretic behavior observed at room temperature of the cobalt ferrite films. Fig. 3 depicts the hysteresis loops recorded at 300 K for two $Co_xFe_{3-x}O_4$ films with $x = 0.05$ and 0.1, respectively. In these plots the magnetization of the films was corrected for the signal of the glass substrate. As seen in both figures, the corresponding loops are not saturated under an applied magnetic field of 1.2 T and, furthermore, no noticeable differences are observed in the coercivity values for the two orientations of the films with respect to the magnetic field.

Such a behavior is indicative of the absence of particular easy axes; combination between the uniform deposition attachment of individual particles to the substrate combined and their randomly oriented easy axes will preclude the existence of an oriented anisotropy in these films. The inset of Fig. 3(a) illustrates the temperature dependence of the coercivity of the $Co_{0.05}Fe_{2.95}O_4$ film as resulted from the measurement with a SQUID magnetometer. The coercivity increases with decreasing the temperature from 3.07 $A\ m^{-1}$ at room temperature up to 16.28 $A\ m^{-1}$ at 5 K. The other structural and magnetic characteristics of the films are summarized in Table 1. A small decrease of the coercivity is noticed upon increasing of the cobalt content; the value measured for $x = 0.05$, that is $H_c \approx 3.07\ A\ m^{-1}$ being similar to that reported for Co-ferrite films processed by sol–gel [15]. However, the coercivity of these films is lower than that of the bulk $CoFe_2O_4$ ($H_c = 6.28\ A\ m^{-1}$) [16], but much higher than that reported for $Co_xFe_{3-x}O_4$ thin films prepared by pulse laser deposition [17] and a modified sol–gel process [18].

The squarness calculated from the data corrected for the demagnetizing field was found to vary only slightly with the composition, having an average value of SQ = 0.64. Also, the saturation magnetization calculated by interpolating the high field values of the magnetization was found to decrease with increasing of the cobalt content of the films from $M_s = 78.8\ A\ m^2/kg$ for $x = 0.05$–68.1 $A\ m^2/kg$ for $x = 0.2$, respectively. Furthermore, for $x < 0.1$ the values of the saturation magnetization M_s are close to the value of $M_s = 80\ A\ m^2/kg$, reported for $CoFe_2O_4$ which indicates that the Co^{2+} ions occupy mainly the octahedral sites and confirms the high quality of these films. In conclusion, highly homogenous, single-phase cobalt ferrite films were deposited by a simple, low-temperature soft solution processing technique. Films with both adjustable thickness and chemical composition are constructed by spherical particles and present a hysteretic behavior at room temperature. While the coercivity is found to increase slightly with the cobalt content, the saturation decreases accordingly, but its values were found to be close to that of the bulk $CoFe_2O_4$, which indicates that the films could be ideal candidates for the design of high density magnetic storage media.

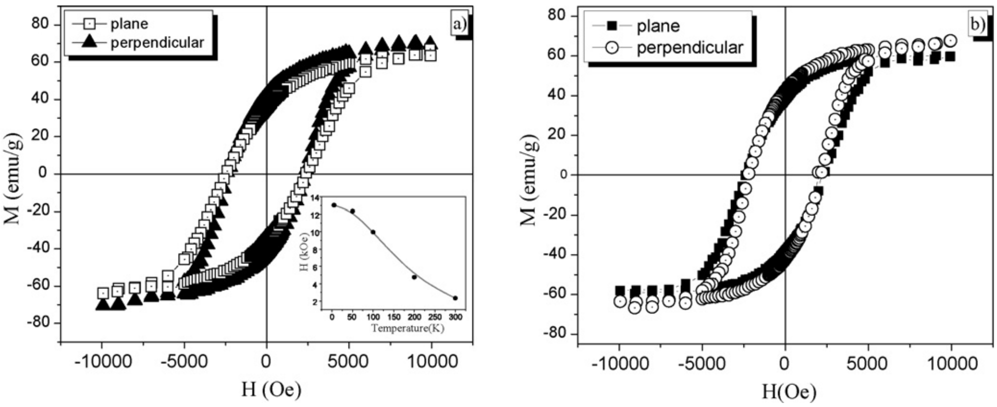

Fig. 3. Room temperature hysteresis loops of $Co_xFe_{3-x}O_4$: (a) $x = 0.05$; (b) $x = 0.1$.

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References

[1] T. Tsurumi, T. Suzuki, M. Yamaze, M. Daimon, Jpn. J. Appl. Phys. 33 (1994) 5192.

[2] H.Y. Zhang, B.X. Gu, H.R. Zhai, M. Lu, Phys. Stat. Sol. 143 (1994) 399.

[3] P.C. Dorsey, P. Lubitz, D.B. Chrisey, J.S. Horwitz, J. Appl. Phys. 79 (8) (1996) 6338.

[4] M. Tachiki, M. Noda, K. Yamada, T. Kobayashi, J. Appl. Phys. 83 (1998) 5351.

[5] H. Itoh, T. Uemura, H. Yamaguchi, S. Naka, J. Mater. Sci. 24 (10) (1989) 3549.

[6] J. Ino, A. Hishinuma, H. Nagayama, H. Kawahara, Japanese Patent 01093443A (Nippon Sheet Glass), June 7, 1988.

[7] Y. Gao, Y. Masuda, T. Yinezawa, K. Koumoto, Chem. Mater. 14 (2002) 5006.

[8] Y. Masuda, T. Sugiyama, K. Koumoto, J. Mater. Chem. 12 (2002) 2643.

[9] Y. Gao, Y. Masudae, K. Koumoto, Chem. Mater. 15 (12) (2003) 2399–2410.

[10] S. Deki, Y. Aoi, J. Mater. Res. 13 (4) (1998) 883;
W. Schiessi, W. Potzel, H. Kartzel, M. Steiner, G. Kalvius, A. Martin, M. Krause, I. Halevy, J. Gal, W. Schafer, G. Will, M. Hillberg, R. Wappling, Phys. Rev. B 53 (1996) 9143.

[11] G. Caruntu, G. Bush, C.J. O'Connor, J. Mater. Chem. 14 (2004) 2753.

[12] R.D. Shannon, C.T. Prewitt, Acta Crystallogr. B25 (1969) 925.

[13] A.R. West, Solid State Chemistry and its Applications, John Wiley & Sons, New York, 1986.

[14] H.P. Klug, L.E. Alexander, X-Ray Diffracton Procedure for Polycrystalline and Amorphous Materials, 2nd ed., Wiley, New York, 1974.

[15] J.G. Lee, J.Y. Park, Y.J. Oh, C.S. Kim, J. Appl. Phys. 84 (5) (1998) 2801.

[16] J. Smit, H.P.J. Wijn, Ferrites, Wiley, New York, 1959.

[17] Y. Suzuki, R.B. Van Dover, E.M. Gyorgy, J.M. Phillips, V. Korenivski, D.J. Werder, C.H. Chen, R.J. Cava, J.J. Krajewski, W.F. Peck, K.B. Do, Appl. Phys. Lett. 68 (5) (1996) 714.

[18] N.C. Pramanik, T. Fujii, M. Nakanishi, J. Takada, J. Mater. Chem. 14 (2004) 3328.