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COFE2O4 AND NIFE2O4 FILM GROWTH AND THE INFLUENCE OF THE MAGNETIC FIELD

Lavkush Kumar

Assistant Professor in Physics RH Govt PG college

kashipur dist us nagar uttrakhand.

ABSTRACT

Functional magnetic materials of composition Ni1-xCoxFe2O4 (x=0, 0.2, 0.4, 0.6, 0.8, 1) were prepared using NiFe2O4 (soft) and CoFe2O4 (semi-hard) nanomaterials following solid state synthesis technique. Magnetic properties of synthesized samples were studied employing XRD, FESEM, VSM and DSC techniques. Curie temperature, Tc of all the samples were determined from the temperature dependence of permeability and compared with the peak temperature of DSC thermograph. Tc is found to decrease with increasing CoFe2O4 substitution which has been ascribed due to weakening of JAB super-exchange interaction between tetrahedral and octahedral sites. The detail hysteresis parameters such as Ms., Mr., Hc have been determined from M-H loop measured at 80, 200 and 300K. Saturation magnetization, Ms measured at 80K was found much higher compared with data at 300K. Ms is found to increase with decreasing temperature and attained a maximum value corresponding to CoFe2O4 at any measurement temperature which may be attributed to higher magnetic moment of CoFe2O4 compared with NiFe2O4. A gradual magnetic hardening was observed to increase with increasing CoFe2O4 content with a maximum value of Hc at x=0.8. Initial permeability as a function of frequency has been measured by an impedance analyzer. Phase transition temperature determined from DSC measurements and temperature dependence of initial permeability was found to display a good correlation. In addition, magnetic hardening of soft NiFe2O4 with increasing amount of CoFe2O4 substitution is also explained based on the existing theories of magnetism.

Keyword :*Cofe2o4 , Nife2o4*

INTRODUCTION

During the last century, spintronics, which deals with the spin-dependent transfer of charge carriers in solids, has been extensively developed. Recently, a new branch of spintronics, straintronics, has emerged studying the effect of elastic deformations caused by external fields on the physical properties of various objects, including materials with a magnetic order. The reflection and absorption of light in magnetic materials depend on magnetic fields and elastic deformations, which makes optical experiments an effective tool for studying electronic, spin, and lattice subsystems, as well as interactions between them and references therein). The fundamental magnetooptical (MO) effects in ferroand ferrimagnets are observed in the range of fundamental absorption near the Curie temperature TC. In this temperature range, the application of a magnetic field gives rise to a significant change in magnetization and thus affects the positions of energy bands. In a magnetically ordered phase, magnetization varies slightly at T << TC and, therefore, MO effects are expected to be weak. However, recent experimental datashowed that the magneto reflection and magneto transmission of nonpolarized light in the ferromagnetic spinel CoFe2O4 at T << TC are sizeable and essentially depend on orientation of the magnetic field applied, thus demonstrating a direct relation with magnetostriction, which is large in this compound Note that in the case of CoFe2O4, the contribution of magnetostriction to the magnetic anisotropy is anomalously large as well A close interplay between MO and magnetoelastic properties in ferrite spinel materials with anomalously strong magnetostriction indicates that such compounds should be considered a special class of optical materials and in the corresponding field of magneto optics can be classified as strain-magneto optics. The literature is scanty for strain-magnetooptical properties of different materials and only CoFe2O4 has been studied so far. However, the matter in question is the discovery of similar properties in magneto strictive magnetic materials of other compositions. In the current work, we review the results of investigations of optical, magnetic and magnetoelastic properties, as well as the effect of magnetostriction on the absorption and reflection of nonpolarized light in the IR spectral range at different orientations of magnetic fields with respect to single crystals of CoFe2O4.

OBJECTIVE OF STUDY

1. A number of applications involving magnetic phenomena require a thin
2. After this nucleation period, the growth is also linea

RESEARCH METHOLOGY /DATA ANALYSICS

A number of applications involving magnetic phenomena require a thin, smooth and conformal magnetic layer fabricated at low temperature, either as a film or within a more complex nanostructure: spintronics, sensing, magnetic storage, and magneto-optics. For this, atomic layer deposition (ALD) would be ideally suited. Indeed, ALD is a thin film technique in which the substrate is alternatively exposed to several gaseous reactants and a smooth conformal film is thereby deposited in layer-by-layer fashion, independently of the substrate's geometric complexity.

Despite this, no ALD reaction of ferro- or ferrimagnetic materials is available to date that simultaneously possesses the following practical advantages: roomtemperature ferro- or ferrimagnetism of the film without further thermal treatment, air stability of the material, use of commonly available precursors, andfast (g0.2 A˚ /cycle) growth of smooth films.2-7 Here,we demonstrate the combination of two wellbehaved binary oxide ALD processes (Fe2O3 and either NiO or Co3O4) to produce the air-stable ferrimagnetic oxides NixFe3-xO4 (nickel ferrite) and CoxFe3-xO4 (cobalt ferrite) directly using ALD. The stoichiometry and thickness of the films are highly controllable, which translates into widely tunable magnetic properties. In particular, we can obtain the stoichiometric MFe2O4, M= Co, Ni.

Among the applications reported for CoFe2O4 are spin valves,8 multiferroic stacks,9 and biomedical ferrofluidics,10 whereas NiFe2O4 is especially suited to microwave applications. The homoleptic cyclopentadienyl complexes of Fe(II), Co(II), and Ni(II) (metallocenes, Cp2M) are combined with ozone for the ferrite ALD reactions. The metallocenes are ideal precursors for ALD—thermally stable, very volatile, reactive to oxidation (to various degrees), commercially available on large scales, and practical to handle. The Fe2O3 ALD reactions based on ferrocene are well-documented between 200 and 500 C and result in deposition rates varying from 0.2 to 1.4 A˚ per cycle.3,12 The ALD process for Co3O4 is usually carried out at slightly lower temperatures (100 to 400C) and results in a deposition rate of 0.5 A˚ per cycle.13 Finally, deposition rates between 3.2 and 0.3 A˚ per cycle are obtained from 150 to 330 C for nickel oxide.2,14

Ozone is chosen in this work as the oxygen source in order to minimize carbon contamination and lower the deposition temperatures.3,12,15 On the basis of the literature reports and our previous studies,2,3,12-14 the deposition of CoxFe3-xO4 is investigated at 250 C and that of NixFe3-xO4 at 200 C in a Savannah reactor from Cambridge Nanotech. The samples were prepared by pulsing ferrocene and ozone, then cobaltocene (or nickelocene) and ozone, on a Si(100) substrate. One ALD supercycle consists of n Cp2Fe/O3 cycles followed by m Cp2M/O3 cycles (M = Co, Ni). This supercycle is repeated until the desired thickness is reached. The ferrocene source was heated at 100 C, cobaltocene at 90 C, and nickelocene at 80 C. The atomic ratio between cations, Fe:M, measured by energy-dispersive X-ray spectroscopy (EDX, Figure 1, open symbols) is almost directly proportional to their corresponding pulse ratios (slopes of ∼0.55 for CoxFe3-xO4 and ∼0.19 for NixFe3-xO4).

The atomic ratio M: Fe in the deposited film is larger than the pulse ratio Cp2M:Cp2Fe for both M= Co and M= Ni. Additionally, the M:Fe ratio in the solid corresponding to any given Cp2M: Cp2Fe ratio in the gas phase is always larger for M = Ni than for M = Co. These observations are consistent with the classic reactivity trend Ni(II,d8) > Co(II,d7) > Fe(II,d6) known for the metallocenes, caused by the antibonding character of the d electrons in excess of 6.16 The growth rate, approximated by X-ray reflectivity (XRR) of a single thick film (g1200 cycles) for every

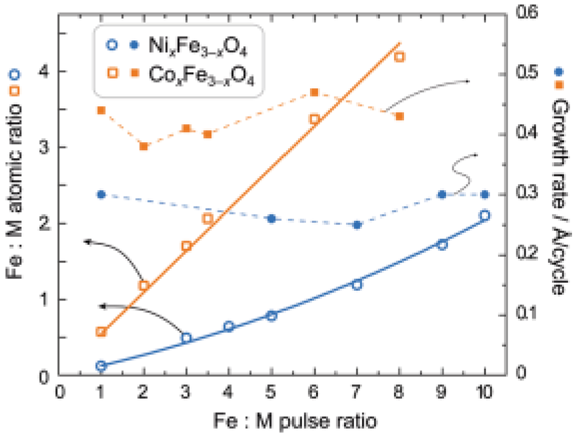

Figure 1. Influence of the ALD supercycle parameters on the composition and growth rate of the MxFe3-xO4 film obtained after g1200 ALD cycles. When a supercycle consisting of n Cp2Fe/O3 cycles and then m Cp2M/O3 cycles is repeated, the Fe:M ratio in the deposited film linearly depends on the n/m ratio, whereas the growth rate remains approximately constant. Blue, M = Ni; orange, M = Co.

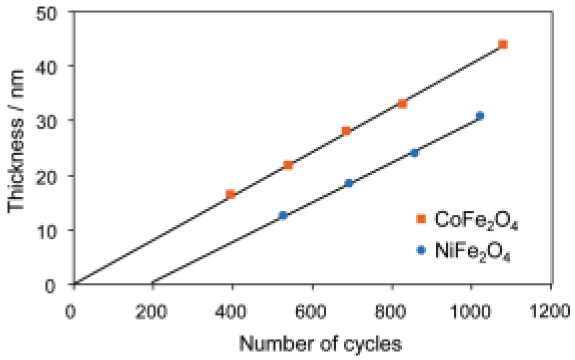

Figure 2. Thickness variation in stoichiometric ferrite films with the number of ALD cycles

composition, is almost independent of the film composition, ~0.3 A˚ /cycle for NixFe3-xO4 and ~0.4 A˚ /cycle for CoxFe3-xO4, (Figure 1, full symbols). The CoFe2O4 thickness deposited depends linearly on the number of ALD cycles performed (Figure 2). In contrast to this, 200 cycles are required for the nucleation of a NiFe2O4 film before the growth starts on the substrate surface. After this nucleation period, the growth is also linear, as shown in Figure 2. Atomic force microscopy (Figure 3) shows that the films deposited are smooth: CoFe2O4 has root-mean-square (rms) roughness of 2 nm and grain size of 30 nm, while NiFe2O4 has 0.7 and 13 nm, respectively. CoxFe3-xO4 samples with various compositions are polycrystalline and exclusively consist of the same spinel phase, as indicated by X-ray diffraction (XRD, Figure 4a).

The corresponding peaks shift to lower angles when the iron concentration increases, indicating that the lattice expands: from 8.24 A˚ (Fe: Co = 0.58) to 8.34 A˚ (Fe: Co= 1.2) then 8.38 A˚ (Fe: Co= 1.7) and finally 8.42 A˚ (Fe: Co = 2), when the (311) reflection is used for calculating the lattice parameter. A similar observation

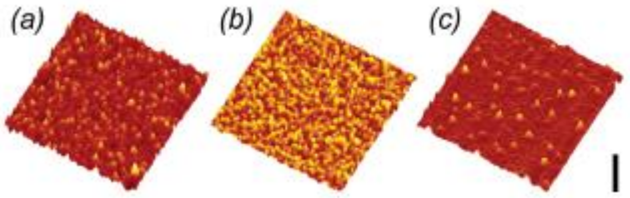

Figure 3. Atomic force micrographs of the film surfaces: (a) CoFe2O4, (b) NiFe2O4 as deposited, and (c) NiFe2O4 after annealing. The areas investigated are squares of (a) 1, (b) 1, and (c) 2.5 µm size; the black vertical scale bar represents (a) 40, (b) 30, and (c) 200 nm, respectively

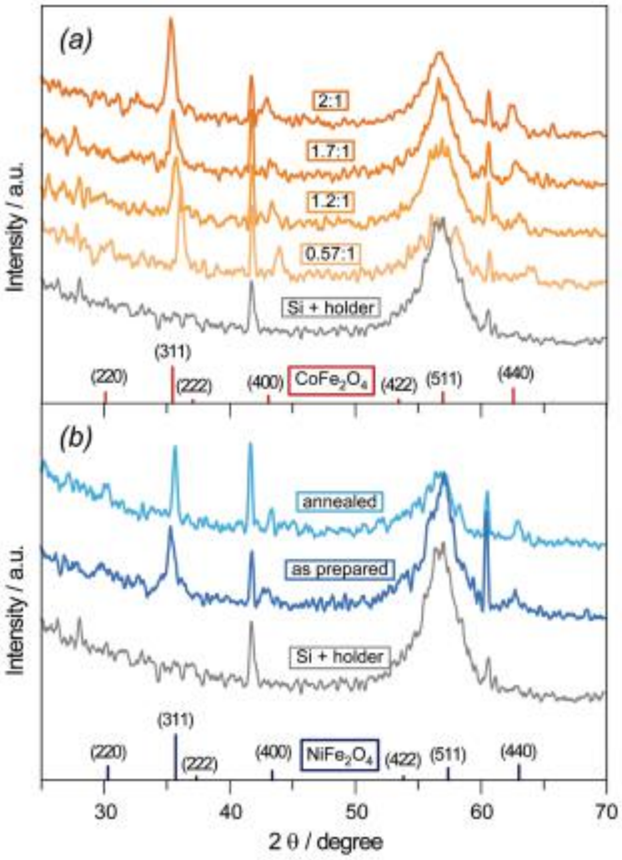

Figure 4. X-ray diffraction of MxFe3-xO4 thin films of various compositions. (a) CoxFe3-xO4 with stoichiometries 1 e x e 2. The JCPDS reference18 for CoFe2O4 is displayed for comparison at the bottom of the graphs. (b) Diffractograms of NiFe2O4 samples before and after thermal annealing, compared to the JPCDS reference

has been reported previously.17 Notably, we are able to modulate the composition between the extremes Co2FeO4 and CoFe2O4 within the spinel phase. The XRD reflections of most as-prepared NixFe3-xO4 samples are weak, revealing that the samples are only partially crystalline. As only member in the series, the NiFe2O4 sample gives rise to stronger signals (Figure 4b). It shows a pure cubic spinel phase, with reflections slightly shifted to smaller angle compared to the JCPDS NiFe2O4 reference.18 Annealing the sample at 700 sharpens the XRD peaks with respect to the as-prepared sample and shifts them to the positions reported for the NiFe2O4 standard. This is consistent with the AFM data of

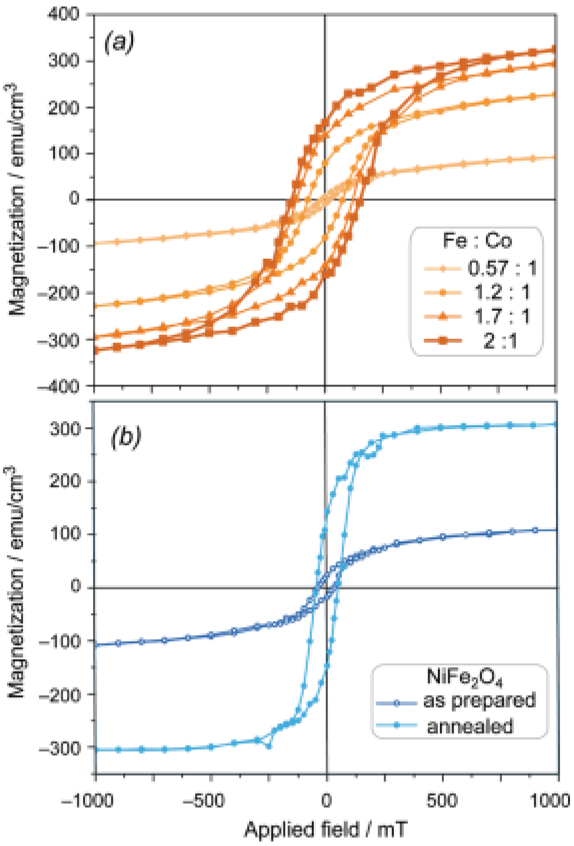

Figure 5. Room-temperature magnetic hysteresis loops of several ferrite films, measured in a magnetic field applied along the sample plane. (a) CoxFe3-xO4 with stoichiometries 1 e x e 2, as deposited. (b) NiFe2O4 before and after annealing

Large crystallites have formed upon annealing of the initially smooth film under AR for 1 h at 700 C (rms roughness 6.3 nm). The magnetic properties of the as-prepared Co ferrite films depend strongly on the Fe: Co atomic ratio, which also determines their crystal structure (Figure 5a). The sample of lowest Fe content has the smallest saturation magnetization (100 emu/cm3) and coercive field (20 MT), corresponding to the Co2FeO4 normal spinel.

From there, both values monotonically increase upon increasing the Fe content: 230 emu/cm3 and 75 MT (Fe:Co = 1.2), 295 emu/cm3 and 122 MT (Fe:Co = 1.7), and finally 325 emu/cm3 and 150 MT for the stoichiometry CoFe2O4. At this point, the saturated magnetization is close to the value of bulk CoFe2O4 (380 emu/cm3).19 Those values remain unchanged after storing the samples in air at room temperature for several months. The high coercive field of 150 MT is the characteristic of the hard magnetic property for which CoFe2O4 is known.

That the saturated magnetization depends on the composition is also typical in this type of ferrimagnets, since the distribution of the various metal ion types between the tetrahedral and octahedral sites of the spinel lattice strongly affects the effective magnetic moment that results in each cell from the sum of ferromagnetic and antiferromagnetic interactions.20,21 Reduced coercivity and remanence are observed for measurements carried out with the magnetic field applied perpendicular to the film surface as compared to the one parallel to the film surface (see the Supporting Information). This suggests that the preferential magnetic orientation of CoFe2O4 is parallel to the film surface, as is the case when shape anisotropy dominates. The effect of the large magneto crystalline anisotropy known for CoFe2O4 is less significant because of the polycrystalline nature and small grain size of the film prepared by ALD.

In contrast to the case of CoFe2O4, the as-prepared NiFe2O4 behaves as a soft magnet with a coercive field of ∼35 mT. Additionally, the saturation magnetization of the thin film is only 110 emu/cm3 (bulk 280 emu/cm3).22 After annealing at 700 C under AR, the saturation magnetization increases to 300 emu/cm3 and the coercive field to 47 MT (Figure 5b). This corresponds to the structural improvements observed by XRD upon annealing. In a control experiment, we have observed only slight changes in the magnetism of CoFe2O4 films after annealing. Thus, cobalt and nickel ferrites thin films are successfully synthesized by combining ALD processes of Fe2O3 and Co3O4or NiO. In each of them, the atomic ratio between the cations can be accurately tuned by controlling the pulse ratio of the corresponding precursors. All samples exhibit a single spinel phase as prepared.

The NiFe2O4 film as prepared has soft magnetic property and weak magnetic signal, further annealing is required to enhance the magnetic signal. On the contrary, stoichiometric CoFe2O4 behaves as a hard magnet and the magnetic signal is strong, as is known for its bulk samples. The magnetic properties of CoxFe3-xO4 samples strongly depend on their compositions. With this, we have the possibility to deposit thin films by an ALD method that combines several advantageous properties. First, the product is magnetic at room temperature without further thermal treatment.

This enables one to capitalize on one major advantage of the thin film technique ALD for applications to thermally sensitive systems, namely its low thermal budget. Second, the films deposited are air-stable, which ensures the stability of the physical properties of the sample or device upon exposure to air. Finally, the precursors are simple, commercially available molecules. Therefore, the technique should prove useful toward applications. Acknowledgment. We thank Prof. A. Cebollada, Instituto de Microelectronica de Madrid-IMM (CNM-CSIC), for performing the XRR measurements and the data analysis, as well as J.M. Montero Moreno and A. Zolotaryov (Hamburg) for their support. We acknowledge funding by the EU via the 7th framework program (project nano MAGMA). Y.T.C. is funded by a fellowship from the DAAD. Supporting Information Available: Experimental section, magnetic hysteresis curves recorded in various orientations, full ref 9 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CONCLUSION

The study of the magnetic, magnetoelastic, optical and magnetooptical properties of single crystals of the ferromagnetic spinel CoFe2O4 highlighted the peculiarities related to the interplay of magnetoelastic and magnetooptical properties of the material. These peculiarities are pronounced in the effects of magneto reflection and magneto absorption (~6% in H~3.5 Koe) of the natural (nonpolarized) light in the infrared spectral range from 1 μm to 30 μm. It was shown that the strain-magnetooptical properties of CoFe2O4 manifest themselves as a correlation of the field dependences of magnetostriction, magneto reflection and magneto absorption. These effects reach large values in the IR range and were ascribed to the sensitivity of the fundamental absorption edge and impurity-absorption bands to magnetoelastic properties of the crystal. The correlation takes place at different orientations of the magnetic field relative to the crystal surface—in the Faraday and Voigt geometries of experiment—and to the crystallographic axes. In the Faraday configuration, a contribution of the Faraday effect to the magneto absorption was observed due to the partial polarization of light in the optical setup. The features of the field dependences of magneto reflection and magneto absorption in the Faraday configuration was related to the additional contribution of mechanical stresses.

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