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Gabriel Caruntu
University of New Orleans, gcaruntu@uno.edu

I Dumitru

Bush GG

Daniela Caruntu
University of New Orleans, dcaruntu@uno.edu

Charles J. O'Connor
University of New Orleans, coconnor@uno.edu

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Magnetic characterization of nanocrystalline nickel ferrite films processed by a spin-spraying method

G Caruntu¹, I Dumitru¹, G G Bush², D Caruntu¹ and Charles J O'Connor¹

¹ Advanced Materials Research Institute, Chemistry Department, University of New Orleans, LA, USA

² Research & Development Division, Lockheed Missiles and Spacer Co., Palo Alto, CA, USA

E-mail: gcaruntu@uno.edu

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Abstract

Highly crystalline nickel ferrite films with different chemical compositions were processed via the spin-spraying method and their morphological, structural and magnetic properties were subsequently investigated. Regardless of the chemical composition, films with variable thicknesses are constructed by 200–400 nm spherical grains grown in the direction normal to the substrate surface. Magnetization measurements show that the spinel ferrite films present a hysteretic behaviour at room temperature with a randomly oriented in-plane easy axis and an anisotropy constant $K_1 \approx -2.5 \times 10^4 \text{ erg cm}^{-3}$. Furthermore, the absence of an angular dependence of the coercivity for the in-plane measurement of magnetization coupled with the 'M'-shaped angular dependence of the out-of-plane measurement, indicates that the anisotropy of this film is predominantly crystalline shape anisotropy.

1. Introduction

Recent trends in the development of microcircuitry have shed new light on transition metal ferrites as potential candidates for the next generation of electronics due to their high chemical stability and tunable magnetic properties. Magnetic semiconductors harbour promise as suitable materials for the design of a large variety of non-reciprocal devices in integrated circuits, reading–writing heads, sensors, catalysts and magnetic recording media. Soft ferrites are particularly important for the further integration of various passive circuit elements in communication devices working in the microwave range. To this end, magnetic materials should possess some key properties, such as high crystallinity, high chemical homogeneity, high magnetic permeability, induced by either a high saturation magnetization or a low uniaxial anisotropy ($H_k = 10\text{--}70 \text{ Oe}$), sufficiently low electrical conductivity and low magnetorestriction. The continuous tendency to miniaturize the electronic circuits has increased the demand

for new materials with improved magnetic properties, and also having small dimensions, such as nanostructured materials or thin films. Although a large number of physical [1–4] or chemical [5–7] methods for the fabrication of magnetic thin films have been devised in the last decade, most of them are multistep synthetic approaches, which require post-synthesis heat treatment in order to ensure good crystallinity of the prepared films.

Recent efforts to obtain new, low-cost magnetic materials possessing features tailorable to various microwave applications have led to a simple, easily scalable and highly efficient one-step low-temperature method, proposed by Abe and co-workers [8]. The so-called spin-spraying method consists of the simultaneous spraying of an oxidizing solution and a treatment solution onto different kinds of substrates mounted on a rotating table. The table is maintained at a constant temperature, usually ranging from 80°C to 90°C. This method is highly desirable for the deposition of transition metal ferrites on heat sensitive substrates, such as plastics or

semiconductors. As part of an effort to expand this method to other metal ferrite films, this paper gives an account of our recent work on the synthesis and characterization of nickel ferrite films with different chemical compositions, obtained by the spin-spraying technique.

2. Experimental details

$\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ films were deposited by the spin-spraying technique at 90°C onto glass and Si substrates under an inert atmosphere of nitrogen. The temperature of the substrates was maintained constant with the help of a temperature controller connected to a thermocouple encased in the rotating table. Prior to deposition, the substrates were degreased and sonicated for 15 min, then rinsed several times and dried at room temperature. Clean substrates were mounted onto the rotating table (200 rpm) and then exposed to two spray solutions. The oxidizing solution contained NaNO_2 (3.7 mmol l^{-1}) and $\text{CH}_3\text{COONH}_4$ (48 mmol l^{-1}), whereas the treatment solution contained FeCl_2 (5.65 mmol l^{-1}) and a suitable amount of NiCl_2 . Accordingly, the concentration of the nickel salt in the treatment solution was varied from 0.25 to 2 mmol l^{-1} . Phase purity of the nickel ferrite films with variable thicknesses was characterized by x-ray diffraction with a Philips X'Pert System equipped with a curved graphite single-crystal monochromator (Cu K_α radiation). Patterns were recorded in a step scanning mode in the $20\text{--}95^\circ 2\theta$ range with a step of 0.02° and a counting time of 10 s. The film composition was determined by both inductive plasma spectroscopy (ICP) and the film morphology was studied with both scanning electron microscopy (SEM) (JEOL 1046) and atomic force microscopy (AFM). Magnetic measurements of the films were performed at room temperature by a vibrating sample magnetometer (VSM, Lakeshore 7300) with a magnetic field up to 1 T. Additionally, x-band ferromagnetic resonance (FMR) experiments were performed with a 9.8 GHz ferromagnetic resonance spectrometer (Bruker EMX 10/12). AFM experiments were carried out in contact mode with a scanning probe microscope (Digital Instruments) equipped with a Si_3N_4 cantilever, with force constant 0.05 N m^{-1} .

3. Results and discussion

Deposition of the nickel ferrite thin films on glass and silicon substrates was achieved via a three-step mechanism, which implies adsorption of transition metal ions to the substrate and partial oxidation of Fe^{2+} ions followed by crystallization of the ferrite film [9]. The oxidizing solution was buffered to a $\text{pH} = 8.5$ by adding a diluted solution of NH_4OH . The x-ray diffraction patterns of the films (not shown) demonstrate that they are single phase with peaks similar to those reported for the spinel-type ferrites. Correspondingly, the x-ray peaks can be indexed into a cubic lattice. In addition, no preferred orientation was detected from the intensity of the x-ray reflections. The thickness of the films was determined by profilometry and found to range between 180 and 480 nm, depending on the deposition time. Figure 1 illustrates the variation of the Ni/Fe ratio as a function of the same ratio in the treatment solution. As seen in the figure, the increase of the Ni content in the reaction solution is accompanied by

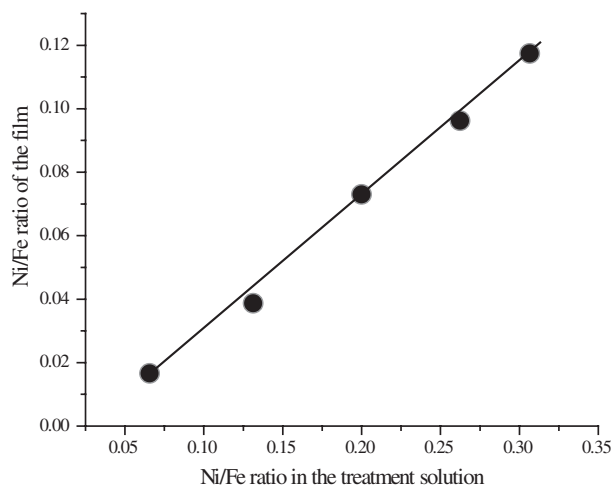


Figure 1. Variation of the Ni/Fe ratio of the films with the Ni content of the treatment solution.

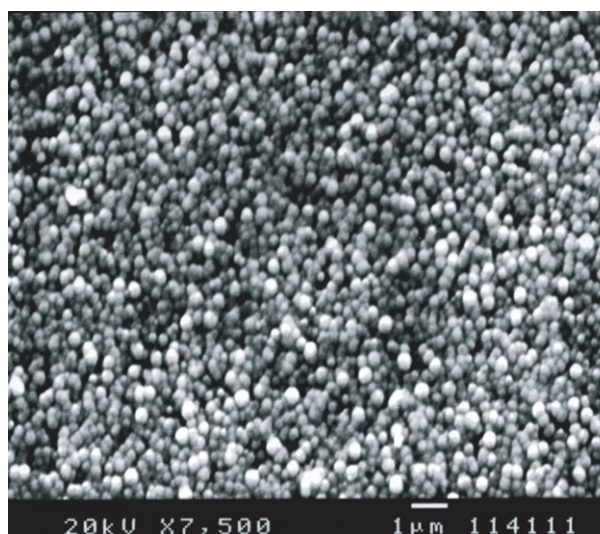


Figure 2. Top view SEM micrograph of the $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film.

a roughly linear increase of the Ni/Fe ratio in the deposited films. However, the Ni incorporation in the films is much lower than that of $\text{Fe}^{2+}/\text{Fe}^{3+}$, which is due to the much higher concentration of Fe^{2+} than Ni^{2+} in the treatment solution. The nickel content of the corresponding films, assuming that the Fe and O compositions are stoichiometric, was found to range between 0.13 and 0.51. The results show that the metal content of the films can be easily controlled through the variation of the transition metal salts in the treatment solution.

Figure 2 shows a representative SEM micrograph of the $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film with a thickness of 400 nm. The experimental data show that regardless of the nickel content, nickel ferrite films are constructed by large arrays of uniform, well-defined spherical grains 200–400 nm in diameter. Thus, our films are much more morphologically homogeneous than ferrite films obtained by the same method [10]. Additionally, the nickel ferrite films presumably possess a columnar morphology [11], undetectable by top view observation during the SEM experiments.

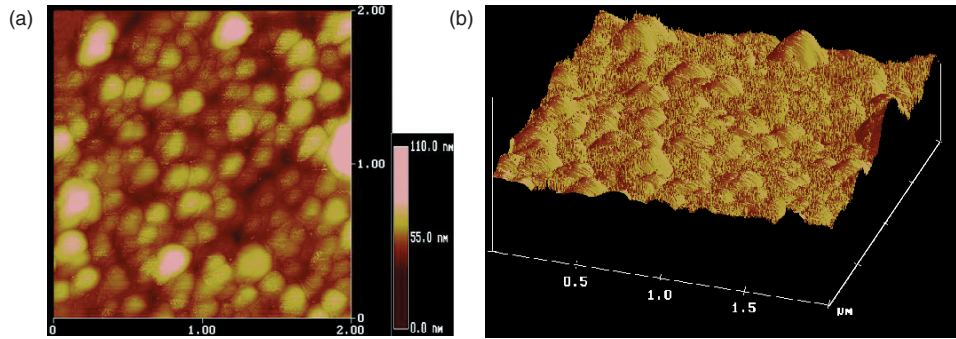


Figure 3. (a) AFM image of the $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film prepared by the spin-spraying technique; (b) 3D view profile of the same film. (This figure is in colour only in the electronic version)

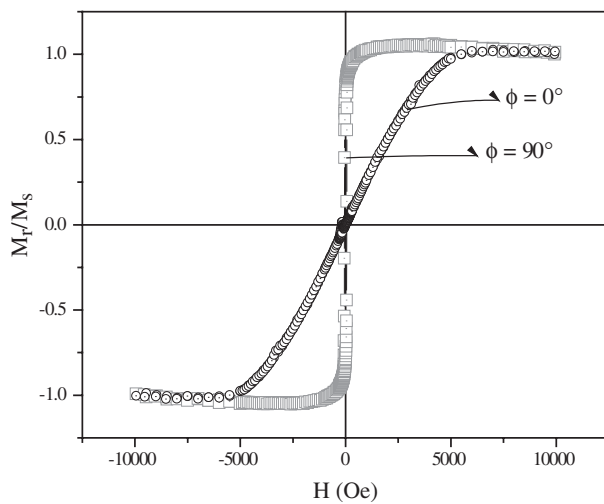


Figure 4. Typical magnetization curve measured at 300 K for the $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film with two orientations of the film with respect to the magnetic field.

The topographical features of the surface of the nickel ferrite films were investigated by AFM. A representative AFM profile corresponding to the $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film with a thickness of 500 nm is displayed in figure 3. The picture reveals a dense film with a good crystallinity constructed by spherical grains with a narrow distribution of size, typically ranging between 200 and 400 nm, grown in the direction normal to the substrate surface.

The data are in good agreement with the experimental SEM observations. Furthermore, the roughness measured in the scan range of $2\ \mu\text{m}$ is about 75 nm, which demonstrates that the deposited films are fairly flat. Magnetic properties were determined at room temperature by applying a magnetic field both parallel ($\phi = 0^\circ$) and perpendicular ($\phi = 90^\circ$) to the normal of the film plane. As seen in figure 4, the hysteresis loops for the two orientations of the field with respect to the film plane have different shapes, which indicate the presence of an in-plane magnetic anisotropy.

The values of the coercivity, squareness ratio SQ ($\text{SQ} = M_r/M_s$), the positions of the FMR peaks, saturation magnetization M_s and anisotropy constant K_1 of the nickel ferrite films investigated are summarized in table 1. According to the experimental data, the squareness, measured in both the in-plane and out-of-plane directions, and the saturation

magnetization M_s decrease with increase in the nickel content, whereas the coercivity of the films remains almost unchanged. Additionally, the squareness measured out of plane is almost three times smaller than that measured in a direction parallel to the film plane. This difference between the squareness values for the two orientations suggests the existence of a planar uniaxial anisotropy.

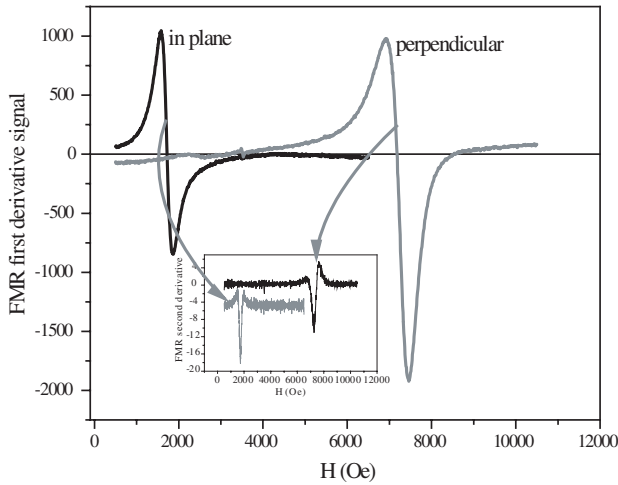
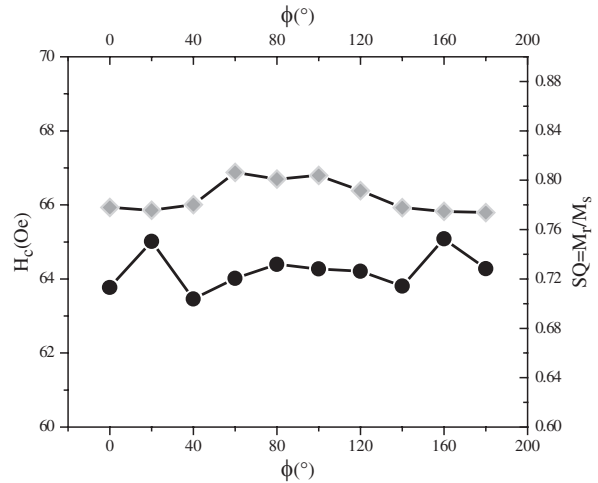
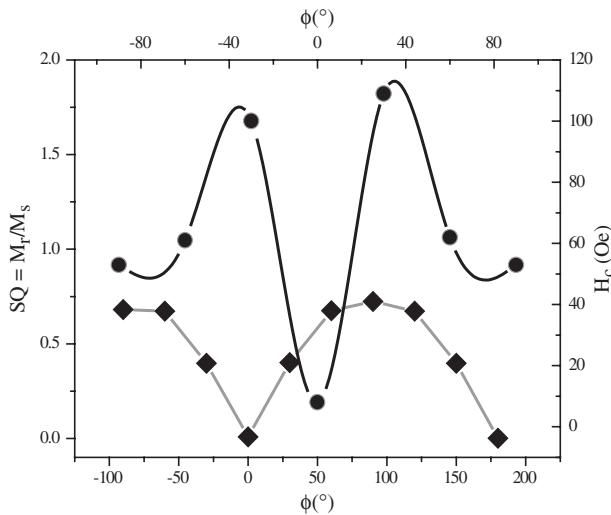
To obtain better insight into the nature of the anisotropy of the nickel ferrite films, FMR experiments were performed at room temperature. As shown in figure 5, all films present distinct resonance peaks for each orientation of the films with respect to the external magnetic field. The linewidth of the resonance peaks were found to vary from 116 to 240 Oe for a parallel orientation of the field with respect to the magnetic field, whereas for a perpendicular orientation they range from 220 to 400 Oe. Additionally, as seen from the second derivative FMR signal (inset of figure 5), the absence of multiple resonances also suggests that the films are magnetically homogeneous [12]. The saturation magnetization is found to decrease monotonically upon increasing the Ni content of the films and the values obtained are in good agreement with the data reported in the literature for thin films and the bulk material [13]. For example, the saturation magnetization of NiFe_2O_4 thin films obtained by a dip-coating process was found to be $196\ \text{emu cm}^{-3}$ [14], whereas NiFe_2O_4 thin films obtained by thermal decomposition of metal acetyl-acetonates have a saturation magnetization of $318\ \text{emu cm}^{-3}$ [15]. Additionally, the values of the anisotropy constant K_1 , calculated from the H_\perp -FMR peaks are very close to the value reported for the bulk material NiFe_2O_4 , namely $-4 \times 10^4\ \text{erg cm}^{-3}$ [16].

Figure 6 shows the angular dependence of the coercivity and squareness, where the abscissa ϕ represents the azimuthal angle between the direction of the magnetic field and the normal to the film surface. As seen in figure 6, in the angular interval of 0° – 90° , the coercivity initially increases from 15 Oe ($\phi = 0^\circ$) to 110 Oe ($\phi = 45^\circ$) and then decreases abruptly to 50 Oe ($\phi = 75^\circ$).

A similar behaviour is observed for angles between 90° and 180° , but in this angular range the maximum of the coercivity reaches about 100 Oe for $\phi = 33^\circ$. Such a 'M'-shaped $H_c(\phi)$ curve follows neither the ideal domain movement mode (a $1/\cos\phi$ curve) nor the Stoner–Wohlfarth rotational mode and could be ascribed rather to a magnetization reversal mechanism occurring by a nucleation and growth

Table 1. Magnetic characteristics of $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ films processed by the spin-spraying method.

Film composition	H_c (Oe)	$(M_r/M_s)_\parallel$	$(M_r/M_s)_\perp$	FMR peak (Oe)			$K_1 \times 10^4$
				H_\parallel	H_\perp	M_s	
$\text{Ni}_{0.05}\text{Fe}_{2.95}\text{O}_4$	73	0.727	0.21	1575	8926	436	-2.32
$\text{Ni}_{0.09}\text{Fe}_{2.91}\text{O}_4$	68	0.681	0.16	1724	7182	299	-2.27
$\text{Ni}_{0.26}\text{Fe}_{2.74}\text{O}_4$	70	0.641	0.12	1666	8056	369	-3.02
$\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$	68	0.659	0.21	1696	7492	324	-2.61

**Figure 5.** FMR peaks for the $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film measured with two orientations of the film with respect to the magnetic field.**Figure 7.** The angular dependence of the squareness and coercivity of a 400 nm $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film rotated in a magnetic field parallel to the film plane.**Figure 6.** The angular dependence of the coercivity (circles) and squareness (squares) of a 400 nm $\text{Ni}_{0.32}\text{Fe}_{2.68}\text{O}_4$ film in a magnetic field making an angle ϕ with the normal of the film.

of reverse domains. These processes can be favoured by both surface irregularities and physical/chemical defects, which, in turn, induce a decrease of the magneto-crystalline anisotropy. Additionally, the M-type $H_c(\phi)$ curve also indicates the existence of an in-plane anisotropy axis [17]. Other systems displaying a similar behaviour were previously reported in the literature and include prismatic Ni nanowires [18], Ni sphere arrays [19] and CoNi films [20]. The corresponding angular

variation of the squareness as illustrated in figure 6 shows a decrease from 0.4 (for $\phi = 150^\circ$) to 0 at the field normal ($\phi = 0$), then an increase to $SQ = 0.7$ when the field is applied parallel to the field plane ($\phi = 90^\circ$) followed by a second decrease to $SQ = 0$ for $\phi = 180^\circ$. Such a $|\cos \phi|$ angular dependence of the squareness also proves the existence of an in-plane uniaxial anisotropy in the nickel ferrite films [20].

However, magnetization measurements when the magnetic field was applied parallel to the film plane, with the film rotating about its own normal, did not reveal noticeable differences between the corresponding hysteresis loops—that is, all in-plane directions are equivalent (figure 7). This indicates that the uniaxial anisotropy that is eventually developed during the film formation is randomly oriented. Consequently, the effect of the centrifugal force acting on the rotating substrate during the film deposition should presumably be considered for the further development of oriented in-plane anisotropy in these films.

4. Conclusions

We prepared highly crystalline nickel ferrite films with different chemical compositions by the spin-spraying method. Highly homogeneous films are constructed by spherical 200–400 nm grains and exhibit room-temperature magnetism with an in-plane easy axis, as confirmed by VSM and FMR experiments. As revealed by the experimental data, the magnetic properties of the samples are mainly dominated by the shape anisotropy. Suitable experiments to further

explore the origin of the anisotropy in the spin-sprayed nickel ferrite films are currently underway and will be presented in a forthcoming paper.

Acknowledgments

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