Effect of growth temperature on the magnetic, microwave, and cation inversion properties on $NiFe_2O_4$ thin films deposited by pulsed laser ablation deposition

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First principles band structure calculations suggest that the preferential occupation of Ni^{2+} ions on the tetrahedral sites in $NiFe_2O_4$ would lead to an enhancement of the exchange integral and subsequently the Néel temperature and magnetization. To this end, we have deposited $NiFe_2O_4$ films on MgO substrates by pulsed laser deposition. The substrate temperature was varied from 700 to 900 °C at 5 mTorr of O_2 pressure. The films were annealed at 1000 °C for different times prior to their characterization. X-ray diffraction spectra showed either (100) or (111) orientation with the spinel structure dependent on the substrate orientation. Magnetic studies showed a magnetization value of 2.7 kG at 300 K. The magnetic moment was increased to the bulk value as a result of postdeposition annealing at 1000 °C. The as produced films show that the ferromagnetic resonance linewidth at 9.61 GHz was 1.5 kOe, and it was reduced to 0.34 kOe after postannealing at 1000 °C. This suggests that the annealing led to the redistribution of Ni^{2+} ions to their equilibrium octahedral sites. Further, it is shown that the magnetically preferred direction of H_a can be aligned perpendicular to the film plane when films are grown with a fixed oxygen pressure of 5 mTorr for films deposited at 700 and 900 °C. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714204]

I. INTRODUCTION

The search for new magnetic materials has been an active research area driven by the development of next generation technologies such as spintronics, magnetoeletric, and monolithic microwave integrated circuits.[1–3] Spinel ferrites have been and remain interesting materials due to valued properties (i.e., high permeability, low anisotropy fields, low conductivity, and moderate magnetization) for microwave applications. Nickel ferrite ($NiFe_2O_4$, Ni-ferrite) possesses comparatively moderate conductivity to most spinels and can perhaps find use in spintronics or high frequency applications.[3,4] Ni-ferrite has been measured to be an inverse spinel at room temperature with Ni^{2+} ions residing on the B (octahedral) sites and Fe^{3+} ions distributed equally among A (tetrahedral) and the remaining B sites. Additionally, Ni-ferrite is known to have low magnetocrystalline anisotropy energy common to cubic magnetic structures[4,5] and relatively low magnetization (~3.4 kG). These less than ideal properties have limited their application in microwave devices.

First principles band structure calculations of Ni-ferrite suggested that if Ni^{2+} ions can be induced to occupy A sites (i.e., a normal cation distribution), then the exchange integral would increase and the Néel temperature and magnetization would be enhanced.[6] It was also experimentally proven in the case of $NiFe_2O_4$ nanoparticles.[7,8] Due to the success of Yang *et al.* in tailoring the cation distribution in the Cu-ferrite system, we were encouraged that the same could be done for the Ni-ferrite system.[9]

In this paper, we present the processing details, structure, and magnetic properties of as-produced and postdeposition annealed Ni-ferrite films deposited by pulsed laser ablation deposition (PLD) technique onto single crystals of (100) and (111) magnesium oxide (MgO) substrates. All films were grown at a fixed oxygen pressure of 5 mTorr at different substrate temperatures. Films grown on (100) MgO showed surface cracks, and the films were peeled off. Consequently, data and analysis for Ni-ferrite films on (111) MgO are presented in this paper.

II. EXPERIMENT

A Ni-ferrite PLD target was prepared by sintering 99.9% pure NiO and Fe_2O_3 starting materials at 1250 °C for 3 h in air followed by ball mill grinding. This process was repeated until a pure phase spinel structure was obtained. Thin films of Ni-ferrite were deposited by PLD onto commercially available (111) plane orientated magnesium oxide (MgO) substrates at 5 mTorr of O_2 pressure. (A Lambda Physik eximer laser with $\lambda = 248$ nm was used for the deposition without a laser energy of 400 mJ and 20 Hz.). The substrate temperatures (T_s) were varied from 700 to 900 °C. A total of 39 600 laser pulses were used, resulting in film thicknesses of approximately 1.4 μm. All the Ni-ferrite films were annealed at 1000 °C in air for each 1 h interval up to a maximum of five-repetitions.

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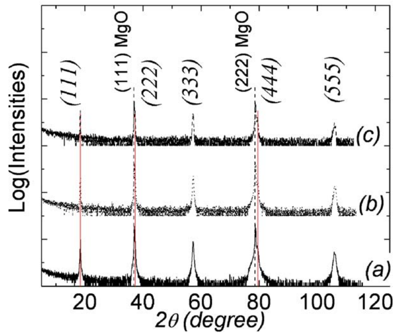

FIG. 1. X-ray diffraction (XRD) spectra of Ni-ferrite films (a) as-deposited at 900 °C, (b) postannealed at 925 °C for 1 h, and (c) postannealed at 1000 °C for 1 h.

All films were examined crystallographically using a Phillips X'pert Pro Multipurpose θ-2θ diffractometer with a Cu K_α target. The thickness of the films was measured by the Dektak meter (Sloan Dektak[3]). A DMS vibrating sample magnetometer (VSM) was used to measure the magnetic hysteresis loops (M vs H) for all the films. From these data we measured coercivity, magnetic anisotropy fields, and saturation magnetization. X-band frequency ferromagnetic resonance (FMR) was performed in both out-of-plane and in-plane FMR conditions by using a TE_{102} rectangular cavity at room temperature. The FMR data allow us to calculate the effective magnetization, anisotropy field, and FMR linewidth.

III. RESULTS AND DISCUSSIONS

As depicted in Fig. 1, Ni-ferrite films grown on (111) MgO substrates were found to have an excellent (111) orientation without measurable impurity phases. The peaks appearing near $2\theta \sim 57°$ and $\sim 106°$ in Fig. 1 do not appear in the reference PDF file,[10] but were readily identified as the (333) and (555) of Ni-ferrite from the measured d spacing and application of Bragg's law.

The lattice parameter deduced for the sample deposited at 700 °C is 8.35±0.01 Å compared to the bulk Ni-ferrite[4] value of 8.42 Å. This represents a contraction of 0.8%; a lattice mismatch of 0.3% is expected between atoms on twice of the MgO (111) plane and those of Ni-ferrite (111). After annealing at 1000 °C the lattice parameter increased to 8.46±0.01 Å, an expansion of 0.5% relative to the bulk value. The lattice parameter of the as-deposited Ni-ferrite films grown at T_s=900 °C was 8.43±0.01 Å with a value of 8.44±0.01 Å after annealing at 1000 °C. In view of the measurement uncertainty, this change is not meaningful. Nonetheless, it indicates that postdeposition heat treatments did not relax the film significantly from its as-deposited state. Alternatively, for the sample grown at 700 °C, the mismatch between the ferrite and the MgO substrate lattice, thermal expansion coefficients, and cation inversion or oxygen deficiency in the film may play a role in straining the ferrite lattice.

From the measured magnetic hysteresis loops, the saturation magnetization $[4\pi M_S = M_S(\text{emu}) \times 4\pi/\text{thickness (cm)} \times \text{surface area (cm}^2)]$ values were measured to be 1960 and 2770 G for the as-deposited Ni-ferrite films grown at 700 and 900 °C, respectively. According to our original hypothesis, this suggests that the as-produced Ni-ferrite films were more inverse spinel than the bulk Ni-ferrite, ($4\pi M_S$ =3770 or 3400 G).[11,12] The density of the as-produced films may not be high enough, and hence the defects can contribute for low $4\pi M_S$ than the bulk.

TABLE I. Static and microwave magnetic properties of PLD Ni-ferrite films grown at 700 and 900 °C followed by annealing at 1000 °C for various durations. ($4\pi M_S$=saturation magnetization, H_c=coercivity, H_a=total anisotropy field, and ΔH=FMR linewidth perpendicular to the film plane)

	As-produced	1 (h)	2 (h)	3 (h)	4 (h)	5 (h)
900 °C						
$4\pi M_S$ (kG)	2.77	2.77	2.79	2.87	3.46	3.42
H_c (kOe)	0.23	0.23	0.30	0.23	0.18	0.22
H_a (kOe)	−1.38	−2.23	−2.39	−2.61	−1.93	−2.14
ΔH (kOe)	1.50	0.45	0.37	0.34	0.34	0.33
700 °C						
$4\pi M_S$ (kG)	1.96	2.15	2.15	1.98	1.95	1.73
H_c (kOe)	0.30	0.30	0.22	0.23	0.16	0.18
H_a (kOe)	⋯	−1.61	−1.65	−2.04	−2.00	−1.99
ΔH (kOe)	⋯	1.89	1.65	1.44	1.26	1.26

The postannealing treatments influenced differently the as-deposited films grown at 700 and 900 °C. The postannealing treatments did not significantly affect the magnetism of the film grown at 700 °C, where the $4\pi M_S$ remained nearly the same (within 10%) for repeated 1 h interval anneals at 1000 °C (Table I). However, the $4\pi M_S$ values for the sample grown at 900 °C continuously increased from 2.7 to 3.5 kG (25% increase) for films deposited at 900 °C by the postannealing up to 4 h. From these results we conclude that only the films at 900 °C experience a cation redistribution induced by the postannealing treatments. Figure 2 shows the hysteresis loops for the Ni-ferrite films after postannealing for 4 hours at 1000 °C. It should be noted that the thickness of the annealed films for various durations at 1000 °C did not change significantly.

The magnetic anisotropy fields were measured by out-of-plane ferrimagnetic resonance at the X-band frequency. Kittel's FMR condition for the out-of-plane measurement can be deduced and written as[5]

$$f_r = \gamma'(H_0 - H_a - 4\pi M_S), \quad (1)$$

where f_r is the resonant frequency, γ' is the gyromagnetic coefficient defined as $\gamma = \gamma'/2\pi$, H_0 is the external magnetic

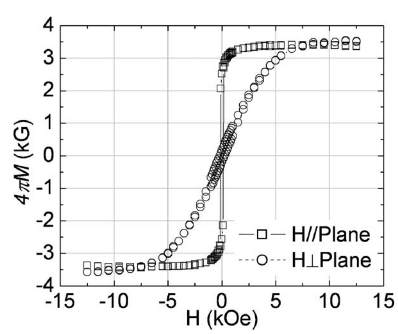

FIG. 2. VSM hysteresis loops for Ni-ferrite films deposited at 900 °C and postannealed for 4 h at 1000 °C.

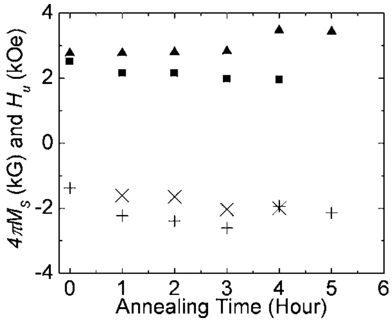

FIG. 3. Uniaxial magnetic anisotropy fields (H_u) and saturation magnetization ($4\pi M_S$) as a function of annealing time at 1000 °C. Triangle (▲) and square (■) symbols indicate saturation magnetization for samples deposited at 900 and 700 °C, respectively. (X) and (+) symbols indicate uniaxial magnetic anisotropy field for films deposited at 900 and 700 °C, respectively.

field perpendicular to the film plane, H_a is the total magnetic anisotropic field, and $4\pi M_S$ is the saturation magnetic field which were measured from the dc hysteresis loops. The H_a in Eq. (1) is called the total magnetic anisotropy field including both uniaxial (growth and postannealing process induced) and cubic contributions, defined as $H_A=-\frac{4}{3}K_1/M_S$ $\sim$400 Oe at room temperature.[12] PLD growth-induced negative anisotropy field in spinel ferrites was reported previously for the Mn-ferrite system.[5] The negative sign of H_a indicated the uniaxial anisotropy field decreased and changed the sign to negative values signaling a spin reorientation to out-of-plane anisotropy. Out-of-plane hysteresis loops in Fig. 2 also showed evidence that the films were having the out-of-plane uniaxial anisotropy such that the loop was saturated at near $4\pi M_S+H_a=5.4$ kOe (see Table I). Since the films have out-of-plane uniaxial anisotropy, the spin reorientation transition may be induced by stress, resulting from the high temperature deposition of ferrites.[13–18] We have estimated the effects of an isotropic tensile planar stress (σ) in films as follows:

$$\sigma \approx -\frac{2}{3}H_u\left(\frac{M_S}{-\lambda_{111}+\lambda_{100}}\right) \approx 18.7\times 10^9 \text{ dyn/cm}^2.$$

where $H_u=[(H_a-H_A)=1600]$, $M_S=3700$, $\lambda_{111}=-21\times e^{-6}$, $\lambda_{100}=-46\times e^{-6}$ for single crystals. This stress corresponds to lattice and thermal expansion coefficient mismatches, and hence the as-deposited films at 700 and 900 °C induce a negative anisotropy field ($-H_A$). Figure 3 shows the uniaxial magnetic anisotropy field and saturation magnetization as a function of postannealing temperature for the as-deposited Ni-ferrite films at 700 and 900 °C. Uniaxial magnetic anisotropy fields with the easy axes perpendicular to the film plane were measured to be $\sim$−2 kOe.

The FMR spectra were measured for the as-deposited and annealed Ni-ferrite films at room temperature and shown in Table I. The FMR linewidths ΔH for the films grown at 700 and 900 °C were measured to be $\sim$2 and $\sim$1.5 kOe, respectively. The ΔH values were correspondingly reduced to 1.2 and 0.34 kOe for the films postannealed at 1000 °C for 5 h. As the tensile stress was estimated for the Ni-ferrite films, we also speculated a greater density of defects for the films deposited at a lower substrate temperature (700 °C) so that the ΔH did not improve upon annealing. However, if the g value for Ni-ferrite is greater than 2, then the stress mechanism or spin orientation in the out of plane will also be an additional factor to have negative H_a. Under the assumption that $g\neq 2$, we were able to estimate g_{eff} value from equating both in-plane and out-of-plane FMR conditions. The g_{eff} values were 2.09 and 2.14 for the films deposited at 900 and 700 °C followed by 5 h of annealing, respectively. The g_{eff} value may also differ with respect to cation inversion[19] in $NiFe_2O_4$.

IV. CONCLUSIONS

Spinel nickel ferrite films were deposited by the pulsed laser ablation deposition technique and showed a reduction in $4\pi M_S$ values of 47%, and 27% in films deposited at 700 and 900 °C, respectively. Films deposited at 900 °C were shown to have an increase in magnetization of 25% by postannealing at 1000 °C in air, and the ferromagnetic resonance linewidth was reduced from 1.5 to 0.34 kOe. The effects of postannealing on the as-produced films at 700 °C were not significant. The negative uniaxial magnetic anisotropy fields (perpendicular magnetic anisotropy field) were measured for all the films and it was found to be $\sim$−2 kOe possibly due to a spin reorientation brought on by stress. We estimate that the films experienced tensile stress which originated from the nonlinear thermal expansion mismatches between Ni-ferrite and MgO substrates and perhaps from lattice defects brought on by nonequilibrium processing.

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