

Magnetic and Structural Properties of RF Sputtered Polycrystalline Lithium Mixed Ferrimagnetic Films

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Compounds with Mn, Ti and Zn have been added to Li ferrite to decrease the magnetic moment of this soft ferrimagnetic compound. Ferrimagnetic compounds with smaller saturation magnetic moments are useful in microwave applications and in high-density recording. These ferrimagnetic films have been deposited on Al₂O₃ polycrystalline substrates at different Ar/O₂ pressures and at different substrate temperatures. Some of the films deposited at lower temperatures in Ar gas only were annealed in oxygen to improve their properties. The magnetic and structural properties of these films depend on the substrate temperature, oxygen partial pressure and the post deposition annealing conditions. The coercivity of films increases with the deposition temperature, oxygen partial pressure, annealing time duration and annealing temperature. The ferrimagnetic films with higher coercivities can be used in high-density magnetic recording media.

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I. Introduction

Previously we have reported on the magnetic and structural properties of rf sputtered non-epitaxial Sr hexaferrite films [1] and rf sputtered polycrystalline Nickel ferrite films deposited on polycrystalline Al₂O₃ substrates [1, 2]. In addition to these, we have deposited easy axis oriented Nickel ferrite films on C-plane sapphire substrates by using the pulse laser deposition (PLD) method [2]. According to our previous studies, the easy axis of hard ferrimagnetic materials such as Sr hexaferrite could be oriented on polycrystalline Al₂O₃ substrates [1], although the easy axis of soft ferrimagnetic materials such as Nickel ferrite could not be oriented on polycrystalline substrates by using rf sputtering [1, 2] or the PLD method [2]. Similarly we could not sputter deposit easy axis oriented films of Lithium mixed ferrite on polycrystalline Al₂O₃ substrates. This implies that the orientation of the easy-axis of soft ferrimagnetic compounds solely depends on the orientation (or type) of substrate.

The formula of Lithium ferrite is Li_{0.5}Fe_{2.5}O₄ (or LiFe₅O₈), which is different from the general form of spinel ferrite MOFe₂O₃. In Lithium ferrite, a quarter of the octahedral Fe⁺³ ions have been replaced by Li [3]. Because there are some vacant sites in the cubic cell, a metal atom of any added material can occupy these vacant sites without changing the cubic structure. But these added materials could change the magnetic moment of a unit cell, and hence the magnetic properties of the ferrimagnetic material. After adding Mn, Ti, and Zn to Lithium ferrite, the

saturation magnetization decreased from 310 to 272 emu/cc. The Lande g factor, resistivity and dielectric constant of this Lithium mixed ferrite are 2.00, 8410 kohms/cm and 14.8, respectively.

Since oxygen ions bombarding on a growing film disrupt the film growth [4-6], these Lithium ferrite films have been deposited by rf sputtering at lower pressures of Ar/O₂. The coercivity of our sputtered films increased with the substrate temperature gradually due to the internal stress of the film [7-9, 12]. The coercivity of Nickel ferrite films deposited by us by using the PLD technique was also higher compared with that of the bulk [2]. The films with larger coercivities are useful in high-density recording media, since the coercivity is directly related to the data storage capacity (or the number of Mega-bytes per unit area) [10, 11]. The coercivity has been further increased in this case, by decreasing the magnetic moment of the ferrimagnetic material [3]. The domain wall resonance takes place at lower frequencies, in the microwave frequency range. This frequency is directly related to the saturation magnetic moment of the material. This frequency can be swept from the microwave frequency range, by using a material with a smaller saturation magnetic moment. So the ferrimagnetic materials with smaller magnetic moments are useful in microwave applications.

II. Experiment

All these films were rf sputtered on polycrystalline Al₂O₃ substrates from custom made Li mixed ferrite bar targets of size 1 cm \times 1 cm \times 4 cm. The side with 1 cm \times 4 cm surface area was facing towards the plasma, since the area of the side facing towards the plasma directly contributes to the deposition rate of the film. These bar targets have been sintered using 74.6% of Fe₂O₃, 8.4% of Li₂CO₃, 2% of MnO₂, 0.2% of BiO₃, 7.4% of TiO₂ and 7.4% of ZnO. If we neglect the very small amount of Bi, then the formula unit of this ferrite can be expressed as (Li_{0.5}Mn_{0.06}Ti_{0.22}Zn_{0.22})Fe_{4.45}O_x. In this sintering process, some of these materials can evaporate more easily than others, and the composition can be slightly different from the above formula unit. So the formula unit can be given as (Li Mn Ti Zn)Fe₅O₈ in the general form of Lithium ferrite. Ar gas has been used as the sputtering gas, and oxygen has been used to fill any oxygen deficiency in the films. The films deposited at lower substrate temperatures without oxygen have been annealed in oxygen to improve the crystallization. If oxygen gas was used during the sputtering, then the films can be directly crystallized at even lower substrate temperatures.

The total pressure of the Ar/O₂ mixture was varied from 15 to 70 mTorr. These films were deposited at substrate temperatures in a range from ambient plasma temperature (63 \pm C) to 770 \pm C. The partial pressure of oxygen during sputtering was changed from 0% to 80%. The percentage of oxygen gas was varied by changing the ratio between the flow rates of Ar and oxygen in this dynamic process. We controlled the amount of Ar and oxygen gases entering into the chamber (flow rates) by using electronic flow controllers. The total rf forward power and the distance from substrate to target were fixed at 150 W and 6 cm, respectively, since the properties of our sputtered ferrite films did not depend on these parameters. The rf bias voltage and the rf reflected power changed in ranges from 1470 to 1270 V and from 16 to 0 W, respectively.

The magnetic measurements including hysteresis loops were measured by using a vibrating sample magnetometer (VSM). All the hysteresis loops in this report are given with substrate corrections. The structural properties of the sputtered films were determined by using a X-ray diffractometer (XRD) with Cu-K α radiation. The thickness, microstructure and including grain size of the sputtered films were investigated by using a scanning electron microscope (SEM). The

compositions of the sputtered films were measured by using a PGT system 4 plus unit coupled to the SEM.

III. Results and discussion

The magnetic hysteresis loop of bulk Lithium mixed ferrite (a piece of our bar target), measured using a VSM, in an arbitrary direction is given in figure 1. The coercivity of this soft Lithium ferrite is very small (5 Oe) according to this graph. The hysteresis loops measured in other directions also showed the same properties, indicating that this Lithium mixed ferrite bar target is isotropic. The coercivity and anisotropy of polycrystalline films sputtered at higher substrate temperatures were much larger than that of the bulk Li mixed ferrite bar. The coercivities calculated from the in-plane and perpendicular to the plane hysteresis loops of a film deposited at $570 \pm \text{C}$ are 200 and 400 Oe, respectively. The hysteresis loops measured in a direction perpendicular to the film plane of two films deposited at $63 \pm \text{C}$ (dashed) and $770 \pm \text{C}$ (solid) in 20 mTorr of Ar are given in figure 2. According to this graph, the coercivity increases with the deposition temperature.

The in plane (solid) and perpendicular (dashed) hysteresis loops of Lithium mixed ferrite deposited at $63 \pm \text{C}$ in 20 mTorr of Ar are shown in figure 3. These two loops nearly overlap on each other, implying that the films deposited at lower substrate temperatures are magnetically isotropic. The coercivity of this film is approximately 20 Oe, which is slightly higher than that of the bulk material. The in plane (solid) and out of plane (dashed) hysteresis loops of a film sputtered at $770 \pm \text{C}$ in 20 mTorr of Ar are shown in figure 4. According to this graph, the film deposited at higher substrate temperature shows some anisotropic properties. The in-plane and out-of-plane coercivities of this film are 280 and 500 Oe, respectively, which are really large compared with that of the bulk. The in-plane coercivity varies linearly with the deposition temperatures as shown in figure 5. All these films were deposited at 20 mTorr of Ar. The slope of this best-fitted line was found to be $0.38 \text{ Oe } \pm \text{C}^{-1}$. The out of plane coercivity also indicated a similar linear variation with the deposition temperature.

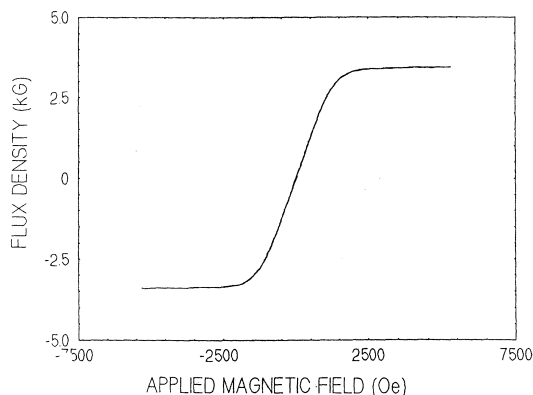


FIG. 1. Magnetic hysteresis loop of bulk Lithium mixed ferrite measured in an arbitrary direction using VSM.

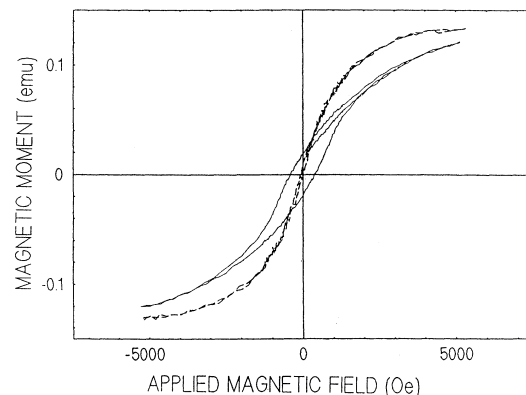


FIG. 2. Out-of-plane hysteresis loops of Lithium mixed ferrite films deposited at substrate temperatures of $63 \pm \text{C}$ (dashed) and $770 \pm \text{C}$ (solid) in 20 mTorr of Ar.

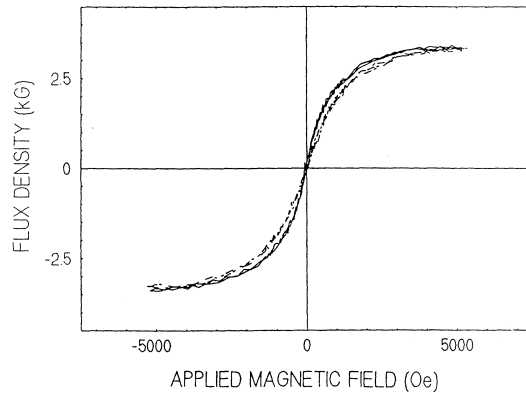


FIG. 3. The in-plane (solid) and perpendicular to plane (dashed) hysteresis loops of Lithium mixed ferrite film deposited at $63 \pm \text{C}$ in 20 mTorr of Ar.

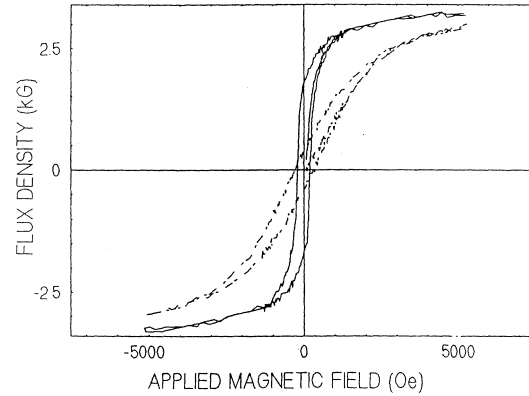


FIG. 4. In-plane (solid) and out-of-plane (dashed) hysteresis loops of Lithium mixed ferrite film deposited at $770 \pm \text{C}$ in 20 mTorr of Ar.

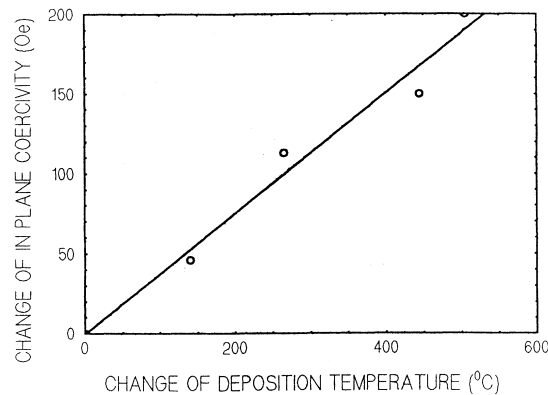


FIG. 5. Graph between the change of in plane coercivity and the change of deposition temperature for rf sputtered Lithium mixed ferrite films.

Because the coercivity changed linearly with the deposition temperature, we can assume that the coercivity increased due to the thermal stress. The origin of the thermal stress is the difference between the thermal expansion coefficients of the substrate (α_s) and the film (α_f). As the film cools down from the deposition temperature to room temperature, the thermal stress arises. The thermal stress also depends on the Young's modulus (E), Poisson ratio (ν), magnetostriction coefficient of the polycrystalline material (λ_s), the difference between the deposition temperature and room temperature (ΔT) and the saturation magnetization (M_s). The stress induced anisotropy (K_u) and the increment of coercivity (ΔH_c) can be given as follows [7, 8, 9, 12]

$$K_u = \frac{3}{2} \lambda_s E \Delta T (\alpha_f - \alpha_s) = 2(1 - \nu);$$

$$\Delta H_c = \frac{3}{2} \lambda_s E (\alpha_f - \alpha_s) \Delta T = (1 - \nu) M_s;$$

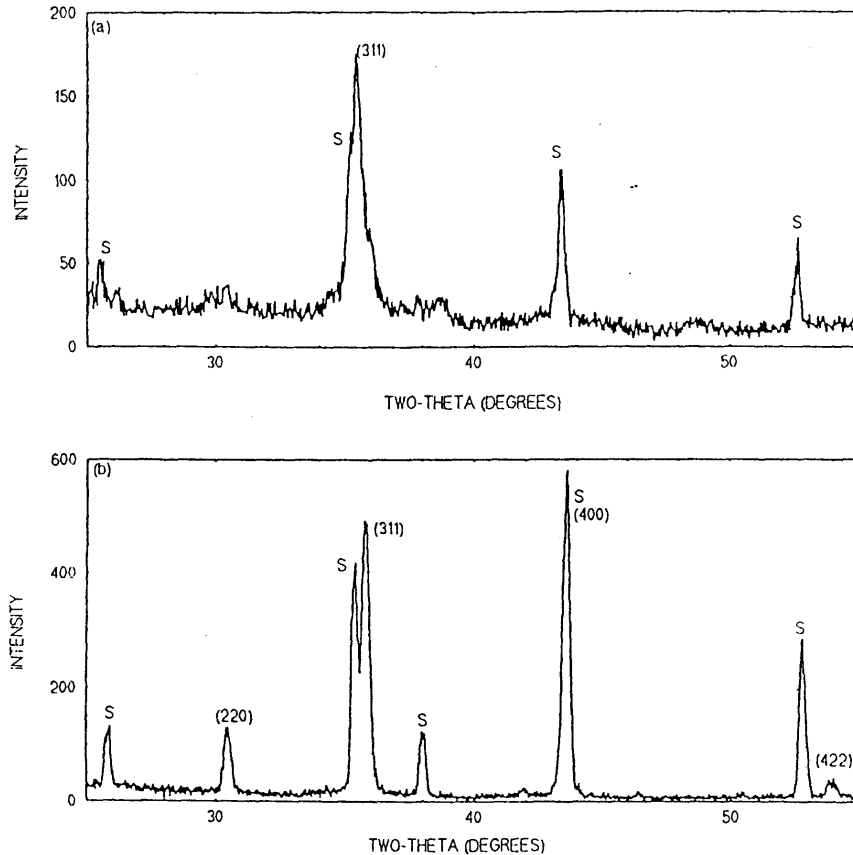


FIG. 6. The X-ray traces of Lithium mixed ferrite films deposited at (a) 70 °C and (b) 570 °C in 20 mTorr of Ar.

According to this equation, the change of coercivity is related to the deposition temperature in a linear manner. The estimated value of the stress induced anisotropy [7-9] of these polycrystalline Lithium mixed ferrite films is approximately 2×10^4 erg/cc at the deposition temperature of 400 °C by using $E = 1.68 \times 10^{12}$ dyne/cm², $\nu = 0.32$, $\rho_f = 1 \times 10^{15}$ Ki⁻¹, $\rho_s = 8.8 \times 10^{16}$ Ki⁻¹ and $\nu_s = 1.2 \times 10^{15}$. This induced anisotropy is significant compared with the crystal anisotropy constants $K_1 = 8.6 \times 10^4$ erg/cc and $K_2 = 2 \times 10^4$ erg/cc. This implies that the stress-induced anisotropy is a crucial factor in the study of soft ferrites [12], although the stress induced anisotropy is smaller compared with the crystal anisotropy for hard ferrimagnetic [1] and rare earth-transition metal (RE-TM) films.

The X-ray traces of films deposited at 70 and 570 °C are given in figure 6(a) and 6(b), respectively. Due to the poor crystallization of the film at the lower deposition temperature (70 °C), only the (311) reflection is visible. (311) is the strongest peak for the powder diffraction pattern of the Lithium mixed ferrite. The intensity of the (311) line is 40% times higher than the intensity of second strongest line (440). As we increased the substrate temperature, we could find different types of XRD peaks. This means that the film can be crystallized well at higher

deposition temperatures. The substrate lines are indicated with “S” in these diffraction patterns, and the (400) peak of the ferrite overlaps with one of the substrate lines.

IV. Conclusion

Some other elements (Mn, Ti and Zn) have been added to Lithium ferrite to decrease the magnetic moment, to make them useful in microwave and magnetic memory applications. The coercivity of Lithium mixed ferrite increased with the deposition temperature due to stress induced anisotropy, similar to the Nickel ferrite films sputtered by us previously [12]. The ferrite films with higher coercivities have some applications in high-density magnetic recording media. The easy-axis of ferrite films can not be oriented on polycrystalline Al_2O_3 by changing sputter parameters according to our studies. Also the films deposited at lower temperatures without oxygen could not be directly crystallized; they could be crystallized only after annealing in oxygen.

References

- [1] H. Hegde, P. Samarasekara and F. J. Cadieu, *J. Appl. Phys.* **75**, 6640 (1994).
- [2] P. Samarasekara, R. Rani, F. J. Cadieu and S. A. Shaheen, *J. Appl. Phys.* **79**, 5425 (1996).
- [3] S. Chikazumi, *Physics of magnetism* (John Wiley and Sons, New York, 1964).
- [4] A. Morisako, M. Matsumoto and M. Naoe, *IEEE Trans. Magn.* **22**, 1146 (1986).
- [5] M. Matsuoka, Y. Hoshi, M. Naoe and S. Yamanaka, *IEEE Trans. Magn.* **18**, 1119 (1982).
- [6] X. Sui, M. H. Kryder, B. Y. Wong and D. E. Laughlin, *IEEE Trans. Magn.* **29**, 3751 (1993).
- [7] P. J. M. VanderStarten, V. V. Banderanko and R. Metselaar, *J. Cryst. Growth* **51**, 119 (1981).
- [8] P. J. Besser, J. E. Mee, P. E. Elkins and D. M. Hienz, *Mater. Res. Bull.* **6**, 1111 (1971).
- [9] J. H. Hsu, C. R. Chang, P. C. Kuo and J. H. Huang, *J. Magn. Magn. Mater.* **89**, 167 (1990).
- [10] E. Murdock, R. Simmons and R. Davidson, *IEEE Trans. Magn.* **28**, 3078 (1992).
- [11] W. D. Chang, T. S. Chin and M. C. Deng, *IEEE Trans. Magn.* **29**, 3682 (1993).
- [12] P. Samarasekara and F. J. Cadieu: *Jpn. J. Appl. Phys.* **40**, 3176 (2001).