OXYGEN PARTIAL PRESSURE DEPENDENCE OF THE COERCIVITY OF SPUTTERED POLYCRYSTALLINE NICKEL FERRITE FILMS

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ABSTRACT

The magnetic properties and structural properties of rf sputtered polycrystalline nickel ferrite ($\text{NiO}:\text{Fe}_2\text{O}_3$) films were investigated. The change of coercivity with the oxygen partial pressure during sputtering is reported in this paper. The coercivity drastically increased from 355 to 1100 Oe as the oxygen partial pressure in the chamber was increased from 6 to 24 mTorr. These films were sputtered on polycrystalline Al_2O_3 substrates in a mixture of argon gas and oxygen gas at one chosen deposition temperature. Since the coercivity depends on the deposition temperature, these films were deposited at one particular deposition temperature. These kinds of ferrimagnetic films with higher coercivities are useful in high-density magnetic recording media.

Keywords: Nickel ferrite films, Magnetic & structural properties, Oxygen partial pressure, rf sputtering, thin films, soft ferrites, coercivity, crystallites

INTRODUCTION

Since 1940, ferrimagnetic compounds have been developed as an important commercial field because of their strong magnetic coupling, high electrical resistivity, low loss characteristics, low cost, chemical stability against environmental corrosion, and mechanical hardness. Most of the research works have been limited to the bulk until the late 1970s. With the development of compact equipments such as computers, calculators, camcorders, cellular phones and satellite communication equipment, a new era of ferrites began. The magnetic thin films of ferrites have received a wide attention after this. Because the capacity of memory devices (or the number of Mega-bytes per unit area) can be increased by increasing the coercivity of ferrimagnetic films, most of the researchers try to make thin films with higher coercivities

nowadays (Murdock, *et al.*, 1992; Chang *et al.*, 1993). But the ferrimagnetic films with smaller coercivities were found to be useful in microwave applications.

Studies on the change of the coercivity with the deposition temperature have already been carried out (Samarasekara & Cadieu, 2001). The coercivity gradually increases with the deposition temperature due to the stress-induced anisotropy in the soft ferrites (Besser *et al.*, 1971; VanderStarten *et al.*, 1981; Hsu *et al.*, 1990; Samarasekara & Cadieu 2001). As the film cools down from the deposition temperature to the room temperature, the film and the substrate contract in different rates because of their different thermal expansion coefficients. Therefore, bending takes place in the ferrite film during the cooling process. This bending gives rise to a definite internal stress of the film. In addition to this, the change of coercivity depends on the stress induced anisotropy, which mainly depends on the Young's modulus, Poisson ratio and the magnetostriction constant of the film material. Also the epitaxial nickel ferrite films deposited on epitaxial substrates using pulse laser deposition (PLD) method had higher coercivities compared with the coercivity of bulk nickel ferrite because of the stress induced anisotropy (Samarasekara *et al.*, 1996).

However, the coercivity changes with the oxygen partial pressure due to a different mechanism. The coercivity of sputter synthesized Sr hexaferrite films increased after annealing in the oxygen (Hegde *et al.*, 1994). Since the filling of the oxygen atoms in the Sr hexaferrite cells increased the directional order, the coercivity increased in that case. However, this theory can't be used to explain the change of coercivity of nickel ferrite in this case. Also the amount of magnetic phases gradually decreased, as the oxygen content of the chamber was increased during the deposition of our earlier Sr hexaferrite films (Hegde *et al.*, 1994). The objective of the present study was to investigate on the change of coercivity of NiFe_2O_4 with the oxygen partial pressure of sputtering chamber.

EXPERIMENTAL

Prior to the sputtering, the chamber was pumped down to a pressure in the range of 10^{-8} Torr, using a system of mechanical pump, cryo pump and ion pump. Then oxygen and argon gases were introduced into the chamber simultaneously using electronic flow controllers. The ratio between the argon and oxygen in this dynamic process was controlled by controlling the gas flow. For example, when the content of oxygen was 50% of total pressure, the oxygen gas flow was exactly the same as the argon gas flow. All films used were deposited on Al_2O_3 polycrystalline substrates. It was possible to crystallize nickel ferrite at very low temperatures when oxygen was

used during sputtering. Therefore, all these films were deposited at 70 °C, which was the ambient temperature of plasma to minimize the effect of the stress on the coercivity. However, the films deposited without oxygen during sputtering were synthesized at deposition temperatures above 223 °C to crystallize the nickel ferrite phase. Because oxygen ions disrupt the film growth at higher pressures (Hegde *et al.*, 1994), films were deposited only at lower pressures in order to obtain smooth films of high quality. Therefore, the films were deposited at 30 mTorr total pressure of argon and oxygen gases.

The nickel ferrite phase of rf sputtered films could be crystallized using custom made nickel ferrite bar targets with stoichiometric composition of NiFe_2O_4 . The size of a bar target was approximately 1 cm X 1cm X 4 cm. The side with larger (1 cm X 4 cm) area was faced to the plasma during sputtering as this area was directly related to the deposition rate of the film. Argon was used as sputtering gas, while oxygen was used to compensate any oxygen deficiency of the film. The substrates were heated using quartz lamps during sputtering. The deposition temperature was measured by a K type thermocouple attached to the back of the substrate. The X-ray diffraction patterns were measured using Cu-K_α radiations. Magnetic measurements were made by means of a vibrating sample magnetometer (VSM). The thickness of the film and the chemical composition of films were measured using a scanning electron microscope (SEM) and a 4 Plus unit coupled to the SEM, respectively.

The coercivity of films was measured based upon the in-plane hysteresis loops performed using VSM. The coercivity of the hysteresis loops measured perpendicular to the film plane also changed in a similar pattern. The total pressure of the chamber was kept at 30 mTorr during sputtering. So when the oxygen partial pressure was changed from 6 mTorr to 24 mTorr, the percentage of oxygen changed from 20% to 80%.

The change of coercivity due to the stress was determined using the following equation (Besser *et al.*, 1971; VanderStarten *et al.*, 1981; Hsu *et al.*, 1990; Samarasekara & Cadieu, 2001).

$$\Delta H_c = 3\lambda_s E(\alpha_f - \alpha_s)\Delta T/(1-\nu)M_s$$

Here λ_s ($= -3.14 \times 10^{-5}$) is magnetostriction constant of the polycrystalline NiFe_2O_4 material, E ($= 1.68 \times 10^{12}$ dyne/cm²) is the bulk Young's modulus of the film material, α_f ($= 1 \times 10^{-5}$ K⁻¹) and α_s ($= 8.8 \times 10^{-6}$ K⁻¹) are the thermal expansion coefficients of film and substrate respectively, ΔT ($= 40$ °C) is the temperature difference between the deposition temperature and the room temperature, ν ($= 0.32$) is the Poisson ratio of NiFe_2O_4 , and M_s ($= 151$ emu/cm³) is the saturated value of the magnetic moment.

RESULTS

The coercivity of the film gradually increased with the oxygen partial pressure in the chamber as shown in Figure 1. The equation of best-fitted curve to the curve given in Figure 1 was found to be $H_c = 541 \ln(p) - 610$. Here, H_c and p denote the coercivity in Oe and the oxygen partial pressure during the sputtering in mTorr, respectively.

Figure 1. Variation of the in-plane coercivity measured by VSM and the oxygen partial pressure during the sputtering in the chamber. All these films were deposited at 30 mTorr total pressure of Ar/O₂ at substrate temperature of 70 °C.

The change of coercivity due to the stress was estimated to be 73.9 Oe. The coercivity of a piece of target material was measured to be 5 Oe using the VSM, as shown in Figure 2. The magnetic field required to saturate the magnetic moment of NiFe₂O₄ is low according to Figure 2. Therefore, this stress induced coercivity is compared with that of the bulk material.

Figure 2. The hysteresis loop of bulk Nickel ferrite in any arbitrary direction as measured by VSM.

The in-plane hysteresis loops of two nickel ferrite films deposited at 20% (solid) and 80% (dashed) of oxygen partial pressures are given in Figure 3. Both these films were deposited at 70 °C in 30 mTorr total pressure without annealing in oxygen. The coercivity of film deposited at 80 % of oxygen was higher compared with that of film deposited at 20%. Here the center parts of the hysteresis loops have been shown in order to indicate the change of coercivity at different oxygen partial pressures clearly. The thickness and the deposition rate of all these films were approximately 1.4 μm and 0.1 $\mu\text{m/h}$, respectively.

Figure 3. The center parts of in-plane hysteresis loops of Nickel ferrite films sputtered at 20% (solid) and 80% (dashed) of oxygen in 30 mTorr total pressure, at 70 °C.

Figure 4. The XRD pattern of a Nickel ferrite film deposited at 70 °C and 50% of oxygen in 30 mTorr of total pressure. Here the XRD peaks indicated by "S" are the substrate peaks.

The X-ray diffraction pattern of a film deposited at 70 °C and 50% of oxygen in 30 mTorr total pressure is shown in Figure 4. This XRD pattern indicates the formation of Nickel ferrite under these conditions. Since (440) is the sharpest peak in the XRD pattern, this peak was selected for line width calculation. The variation of linewidth of (440) peak of XRD patterns of films deposited at a total pressure of 30 mTorr and a temperature of 70 °C with the oxygen partial pressure is given in Figure 5. The linewidth gradually increases with the oxygen partial pressure from 6 to 24 mTorr. This implies that the particle size gradually decreases with the oxygen partial pressure of the chamber during sputtering.

Figure 5. The variation of graph between the linewidth of (440) peak and the oxygen partial pressure.

DISCUSSION

The coercivity of a magnetic material depends on following factors: (1) the internal stress (Besser *et al.*, 1971; VanderStarten *et al.*, 1981; Hsu *et al.*, 1990; Samarasekara & Cadieu, 2001) (2) the saturated value of magnetization (Chikazumi, 1964; Matsushita & Naoe, 1993) (3) the magnetocrystalline anisotropy (Chikazumi, 1964; (Morisako *et al.*, 1987; Morisako *et al.*, 1988) and (4) The size of particles (or crystallites) (Williams *et al.*, 1949; Nesbitt, 1950; Chikazumi, 1964). The effect

of stress on the coercivity has been described earlier. If the saturated value of magnetization is smaller (Matsushita & Naoe, 1993) or larger compared to that of bulk, then it could be increased or decreased by annealing in oxygen. The coercivity increases as the saturated value of magnetization decreases (Chikazumi, 1964). As the oxygen partial pressure is increased during sputtering, the magnetocrystalline anisotropy increases due to the filling of oxygen atoms in the unit cell (Morisako *et al.*, 1987; Morisako *et al.*, 1988). This same phenomenon takes place during annealing in oxygen atmosphere. The coercivity also increases with the magnetocrystalline anisotropy (Chikazumi, 1964). The coercivity increases as the size of crystallites is decreased. If the size of crystallites is small enough to make single domain particles, then the coercivity reaches its maximum possible value (Williams *et al.*, 1949; Nesbitt, 1950; Chikazumi 1964).

Since the change of coercivity with the oxygen partial pressure during the sputtering is considered, attention has to be paid in this study, to the effect of magnetocrystalline anisotropy and the effect of particle size also. The oxygen atoms in the plasma become oxygen ions (O^{+2}) due to the thermal collisions between atoms. These oxygen ions accelerate toward the sample due to the strong repulsive force exerted on them by negatively charged cathode (or target). Therefore, these high energetic oxygen ions collide on the growing film, and interrupt the film growth (Morisako *et al.*, 1986). Hence, the size of the particles in the growing film became smaller as the oxygen partial pressure was increased, and the coercivity of the sputtered nickel ferrite films increased with the oxygen partial pressure.

Some other researchers have noticed that the width of XRD peaks increases as the particle size decreases for sputtered barium hexaferrite films at different oxygen partial pressures (Morisako *et al.*, 1986; Morisako *et al.*, 1987; Morisako *et al.*, 1988). According to their studies, the coercivity and the XRD line width increased with increasing partial pressure of oxygen during sputtering. Therefore, it can be hypothesized that there is a direct relationship between the coercivity and the particle size in soft ferrites such as nickel ferrite. Most of the researchers sputter deposit ferrite films at smaller oxygen partial pressures because of this reason.

According to thermodynamics, the Helmholtz free energy (F) of a system varies with the pressure in the following manner.

$$F = CT \ln(p) + \text{constant}$$

Here C is a constant and T is the absolute temperature of the system. It is reasonable to assume that this free energy of an oxygen ion is completely transferred to the film, as the oxygen ion collides with the film. Because these colliding oxygen ions are capable of breaking the crystallites into parts, the size of crystallites

decreases with the free energy of oxygen gas. The energy achieved by oxygen ions during acceleration in the electric field produced by the bias voltage of the target can be considered as a constant, since these ions travel a very small distance (1 - 4 mm) between the plasma and the substrate.

The energy required to break a crystallite also depends on the strength of bonding between molecules. This binding energy is almost constant for the considered material. The temperature of the plasma is also constant as long as the bias voltage and the substrate temperature are kept constant. Since the coercivity gradually decreases with the size of a crystallite (Kittel, 1948) and the size of crystallite gradually decreases with the free energy of the oxygen gas, there must be a direct relationship between the coercivity and the free energy of the system. Therefore, the above thermodynamical model agrees with the results given in Figure 1.

CONCLUSIONS

The coercivity of sputtered nickel ferrite films change with the oxygen partial pressure in the chamber (up to 80% of oxygen in 30 mTorr total pressure), as measured by VSM. A logarithmic relationship exists between the coercivity and the oxygen partial pressure. Since the oxygen ions continuously bombard on the growing film, the size of crystallites becomes smaller with the oxygen partial pressure. Although the films have been sputtered at lower deposition temperatures to minimize the effect of internal thermal stress on the coercivity of the films, raising the deposition temperature and the oxygen partial pressure simultaneously will increase the coercivity of films drastically as recorded by Samarasekara & Cadieu (2001). The ferrimagnetic films with higher coercivities have some applications in high-density magnetic recordings.

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