Effect of Co/Sn Doping on the Thermal Stability of Magnetic Properties of Ba-Ferrite Thin Films

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Abstract—$BaFe_{12-2x}Co_xSn_xO_{19}$ (where x=0 ~ 1.03) thin films were made by rf magnetron sputtering in Ar-O_2 mixed atmosphere. These films were then post-annealed in air between 850℃ and 1000 ℃ for 10 minutes, in order to get M-type phase. The contents of Co/Sn on the magnetic properties and thermal stability of the magnetic properties of the films were discussed.

I. INTRODUCTION

Recently, there has been interested in using thin film BaM for high density magnetic recording media, because it possess not only excellent magnetic properties but also has good mechanical and chemical stability. Sputtered Ba-ferrite thin films under normal conditions are amorphous structure in nature and they are nonmagnetic [1]. Hence, crystalline BaM thin films have to be obtained by either applying in-situ substrate heating during deposition [2] or through a post-deposition annealing treatment [3].

Many investigators [4-6] indicate that Co/Ti doped BaM particles could reduce grain size of the particles. However, their temperature coefficient of coercivity dHc/dT is about +3~+4Oe/℃ [7]. Kubo et al. [7] have substituted various third elements into the Ba-ferrite particles. They found that Sn is the most effective element in reducing dHc/dT of the particles. Li and Sinclair [8] found that temperature coefficient of coercivity dHc/dT of the Ti/Zn doped BaM thin film is about +0.5 Oe/℃ for perpendicular coercivity and -3Oe/℃ for in-plane coercivity.

In this report, we investigate the effect of Co/Sn doping on the thermal stability of the magnetic properties of the BaM films. The effects of Co/Sn contents and annealing temperature on the perpendicular and in-plane magnetic properties of the Co/Sn doped BaM thin films were also examined.

II. EXPERIMENT

$BaFe_{12-2x}Co_xSn_xO_{19}$ (where x=0 ~ 1.03) thin films were made by rf magnetron sputtering system in the Ar - O_2 mixed atmosphere, then post-annealed in air between 850℃ and 1000℃ for 10 minutes. Co/Sn doped BaM targets were used in this experiment. All of the films were deposited onto a room-temperature fused silica glass substrate. The base pressure in the system was 1×10^{-5} Torr, and after the high purity Ar-O_2 mixed gas (Ar : O_2 = 9 : 1) was introduced, sputtering pressure was 5×10^{-3} Torr. Thickness of the films was 100 nm.

The structure and phase types of the films were determined by using x-ray diffractometer (XRD). Magnetic properties of the films were measured with vibrating sample magnetometer (VSM) at room temperature with maximum applied field of 12 kOe. Composition and homogeneity of the films were determined by energy disperse x-ray spectrometer (EDS). Thickness of the films was measured by a α-step.

III. RESULTS AND DISCUSSION

Figure 1 shows the coercivity Hc and saturation magnetization Ms of the $BaFe_{12-2x}Co_xSn_xO_{19}$ thin films as a function of Co/Sn content x. These films were post-annealed at 950℃ for 10 minutes in air. It can be seen that both the out-plane coercivity $Hc_\perp$ and in-plane coercivity $Hc_\parallel$ decrease dramatically with increasing x while the saturation magnetization Ms decreases slowly with increasing x. For pure BaM film, its $Hc_\perp$ is about 3200 Oe, $Hc_\parallel$ is about 2200 Oe, and Ms is about 320 emu/cm^3. As x is increased to 0.83, they decrease to about 1100 Oe, 850 Oe, and 240 emu/cc, respectively for x=0.83. The out-plane coercivity always higher than that of in-plane for the same x. The increasing of Co/Sn content x will suppress the out-plane coercivity more than that of the in-plane coercivity. Hence, we can get nearly magnetic isotropy BaM thin films (i.e., $Hc_\perp \cong Hc_\parallel$) by doping proper amount of Co/Sn.

The magnetic moment of Ba-ferrite unit cell is coming from the resultant moment of Fe^{3+} ions at spin-up (12k,2b) and spin-down ($4f_2$) sites [9]. The decrease of Ms value with increasing x is due to that the substitution of these magnetic Fe^{3+} ions with nonmagnetic Sn^{4+} ions. On the other hand, the Fe^{3+} ions at 12k and 2b sub-lattices are major contributors to the overall uniaxial anisotropy of BaM ferrite [10]. The substitution of Fe^{3+} ions with Co^{2+} and Sn^{4+} ions at 12k and 2b

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sites will destroy the exchange interaction between adjacent 12k and 2b sites and reduce the coercivity of BaM .

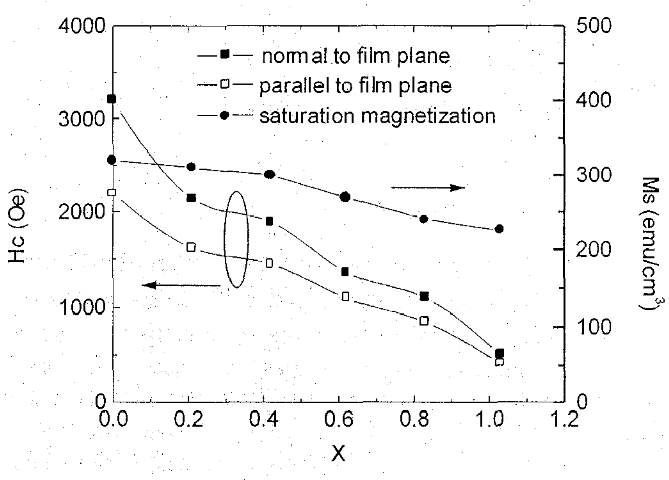

Fig. 1. Coercivities and the saturation magnetization Ms as function of Co/Sn-doping x for the $BaFe_{12-2x}Co_xSn_xO_{19}$ thin films. These films were post-annealed at 950℃ for 10 minutes in air.

Figure 2 shows the variation of Ms with temperature between 20℃ and 100℃ for various $BaFe_{12-2x}Co_xSn_xO_{19}$ thin films. It is obviously that the value of Ms decreases with increasing temperature. In figure 2, we can see that the slope of Ms vs. T curve is decreased with increasing x. This is due to that the variation of Ms with temperature is dominated by the interactions of 12k-2a ions and 12k-12k ions for small x (x=0~0.42). But, it is dominated by the perturbing effect of 12k-2b interaction for larger x (x=0.62~1.02) [11].

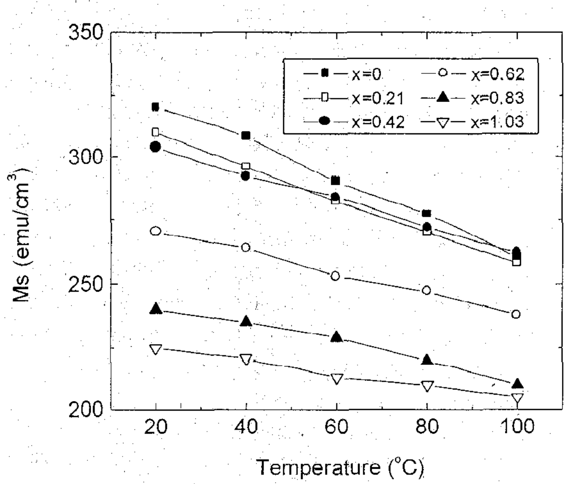

Fig. 2. The Ms value of $BaFe_{12-2x}Co_xSn_xO_{19}$ thin films as function of temperature between 20℃ and 100℃.

The temperature coefficient of coercivity, defined by dHc/dT, was determined as dHc/dT = ［Hc (100℃) – Hc (20℃)］/ 80℃. Where Hc (100℃) and Hc (20℃) are the coercivities at 100℃ and 20℃, respectively. The values of dHc/dT as a function of x for the $BaFe_{12-2x}Co_xSn_xO_{19}$ thin films are plotted in figure 3. These curves indicate that both in-plane and out-plane coercivities are increased with increasing temperature for $x < 0.62$, and decreased with increasing temperature for $x > 0.62$. The dashed line indicates that the coercivity is not affected by the temperature. The out-plane dHc/dT of the film is decreased from +4.2 to –1.3 Oe/℃ and out-plane dHc/dT decreases from +4.8 to –1.1, as x increase from 0 to 1.03. For x=0.62, the values of out-plane and in-plane dHc/dT are 0.1Oe/℃ and 0.2Oe/℃, respectively.

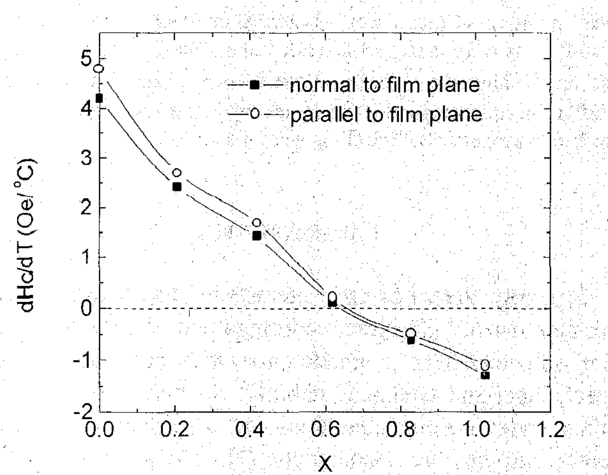

Fig. 3. The temperature coefficient of coercivity dHc/dT as function of x for various $BaFe_{12-2x}Co_xSn_xO_{19}$ thin films.

Figure 4 shows X-ray diffraction patterns of the $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ films which annealed at temperatures between 850℃ and 1000℃ for 10 minutes in order to avoid grain growth. It reveals that completely M-type Ba-ferrite can be obtained when the annealing temperature T_A is higher than 950℃. As T_A is lower than 900℃, we can see that there has nonmagnetic α-Fe_2O_3 phase appeared.

Figure 5 shows the variations of Hc and Ms of the $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ thin film with annealing temperature between 850℃ and 1000℃. Ms is increased with annealing temperature T_A and the increase of Ms becomes slowly as T_A >950℃. Hc is also increased with T_A as T_A is lower than 950℃, but it decreases when T_A is higher than 950℃. When T_A <950℃, the increase of Ms and Hc with T_A is due to the decrease of nonmagnetic amorphous phase and α-Fe_2O_3 phase as shown in Fig.4. As T_A is higher than 950℃, the decrease of Hc is due to rapid grain growth of the film, as shown in figure 6. Figure 6 shows the variation of average grain size of the $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ thin film with T_A. It can be seen that the average grain size increases slowly from 12nm to 20nm when T_A is increased from 850℃ to 950℃, and it increases rapidly as T_A >950℃. The average grain size was calculated from scherrer formula [12] with half-maximum peak width of the main peak (008) in figure 4.

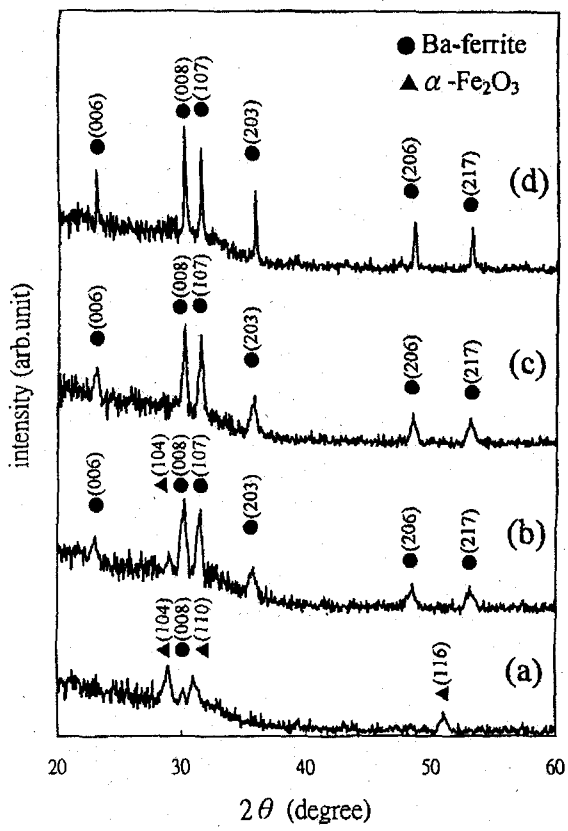

Fig. 4. X-ray diffraction patterns of the $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ thin films which are annealed at various temperatures: (a) 850℃; (b) 900℃; (c) 950℃; (d) 1000℃.

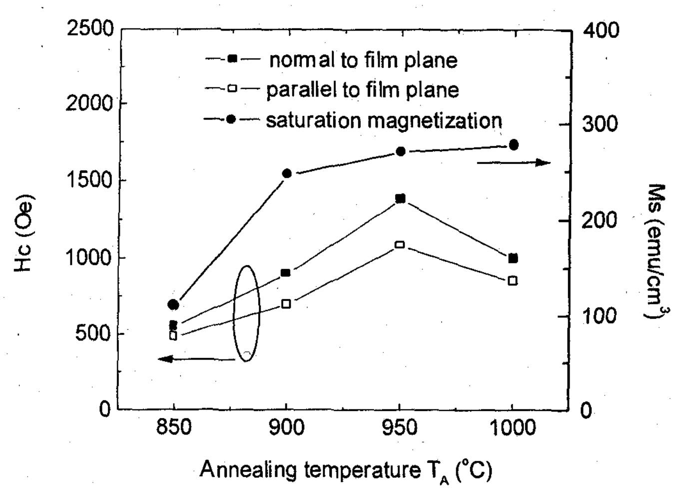

Fig. 5. Coercivities and the saturation magnetization as function of annealing temperature for the $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ thin films. These films were post-annealed for 10 minutes in air.

IV. CONCLUSION

The Co/Sn doped barium ferrite (BaM) thin films had been prepared by using rf magnetron sputtering. Ms, $Hc_{\perp}$, and $Hc_{\parallel}$ of the film was decreased with increasing Co/Sn concentration. For the $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ thin film, both in-plane and out-plane coercivities almost keep constant with temperature between 20 ℃ and 100 ℃. Its out-plane coercivity is about 1400 Oe and in-plane coercivity is about 1100 Oe. The saturation magnetization Ms is about 270 emu/cm^3 and the average grain size is about 20 nm. It reveals that this $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ thin film has excellent magnetic thermal stability.

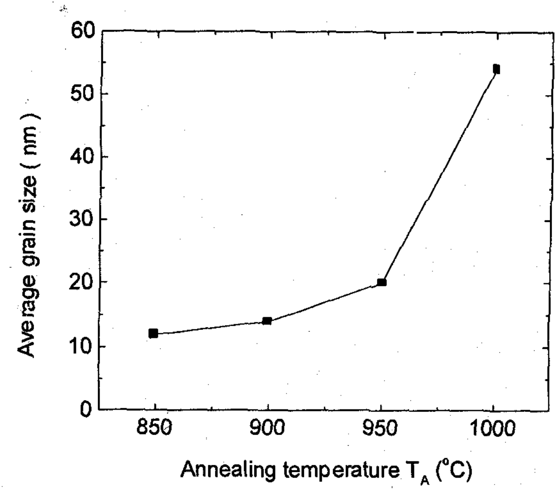

Fig. 6. Average grain size as function of annealing temperature for the $BaFe_{10.76}Co_{0.62}Sn_{0.62}O_{19}$ thin films. These films were post-annealed at 850℃ ~1000℃ for 10 minutes in air.

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