High Coercivity and High Saturation Magnetization Mn-Al Thin Films

J. H. Huang, P. C. Kuo and S. C. Shen

Abstract—**Mn-Al thin films with the composition of 31–68 at.% Mn were prepared by rf magnetron sputtering at various substrate temperature then annealing in vacuum. Effects of the chemical composition, substrate temperature and annealing temperature on the magnetic properties of Mn-Al films have been investigated. The analysis of x-ray diffraction and magnetic measurement indicate that τ-phase was synthesized at a composition range of 40–60 at.% Mn. However, the formation of large amount of τ-phase occurred at Mn_{50}-Al_{50} films, which have a high coercivity up to about 3000 Oe and a fairly large saturation magnetization of about 420 emu/cc.**

I. Introduction

THE existence of a ferromagnetic phase in the Mn-Al system containing about 45 ~ 58 at.% Mn is a result of the metastable τ-phase, the structure and magnetic properties of which have been extensively investigated [1]–[7]. This ferromagnetic τ-phase has a tetragonal $L1_0$ type superstructure and high crystalline anisotropy energy as large as about 10^7 erg/cc. The ferromagnetism of the τ-phase occurs because the magnetic moments of Mn atoms in 0, 0, 0 sites are parallel to one another. The disorder in the τ-phase structure may cause the Mn atoms move into 1/2, 1/2, 1/2 sites, and the Mn atoms in 0, 0, 0 and 1/2, 1/2, 1/2 sites are coupled antiferromagnetically [2]. Many mechanisms have been proposed for the τ-phase formation [8, 9]. The usually accepted mechanism is that the high-temperature non-magnetic ϵ-phase (hcp) transforms into a non-magnetic ϵ'-phase (orthorhombic) by an ordering reaction, then transforms into a metastable ferromagnetic τ-phase (fct) by a martensitic mode.

Metal thin films have been developed for recording media to cope with the ever-increasing demand of high density recording. Among them, Co-based alloy films have come into practical use. Preparation of τ-phase in Mn-Al films and their magnetic properties have been investigated by Morisako and Matsumoto [10]. According to their reports, ferromagnetic τ-phase of Mn-Al binary alloy films were synthesized at Mn content of about 60 at.% and substrate temperature of about 150°C. However, since these films exhibited low saturation magnetization Ms of about 120 emu/cc, which is only one-fourth of the bulk material, they were not applicable for the magnetic recording media. Further investigations were studied by doping the elements such as, Cu, Ni, Fe, Co, Ag, Zn [11]–[14]; they found a maximum saturation magnetization of about 300 emu/cc for a Mn_{38}-Al_{40}-Cu_{22} film. However, the coercivity decreased to about 220 Oe. These films were composed of both the Mn-Al τ-phase and Mn-Al-Cu κ-phase. The single ferromagnetic τ-phase has not been fabricated before.

In this paper, we report the effects of the chemical composition, substrate temperature and annealing temperature on the magnetic properties and formation of ferromagnetic τ-phase of Mn-Al films. A nearly single phase of ferromagnetic τ-phase with good magnetic properties was produced in this study.

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II. Experimental

The films have been deposited by means of an rf magnetron sputtering system. A mosaic target consisting of a high purity aluminium disk (99.999%) overlaid with small high purity manganese pieces (99.99%). This arrangement provides a wide range of effective target compositions and therefore films compositions. Films were deposited on glass substrates at substrate temperature Ts ranging from 30 to 250°C.

Applied rf power source was working at 80W and a typical deposition rate was 0.5 nm/s. The base pressure in the system was 5×10^{-7} Torr, and after the high purity Ar gas was introduced, the sputtering pressure was set at 1 mTorr. Films in thickness of 0.8 μm were used in this study. Thermal annealing was carried out at temperature range between 350 and 550°C in vacuum.

Crystal structures of the deposited films were characterized by x-ray diffractometer (XRD) and their compositions were determined by electron probe microanalyzer (EPMA) calibrated by a standard of Mn_{55}-Al_{45} alloy. Magnetic properties of the films were measured with vibrating sample magnetometer (VSM) at room temperature in the maximum applied field of 10 kOe.

III. Results and Discussion

The Mn-Al films with Mn concentrations ranging from 31 to 68 at.% were produced, their magnetic properties were measured to examine the existence of the τ-phase. The films were deposited at substrate temperature (Ts) of 30°C and then annealed at 410°C for 30 min. Fig. 1 shows

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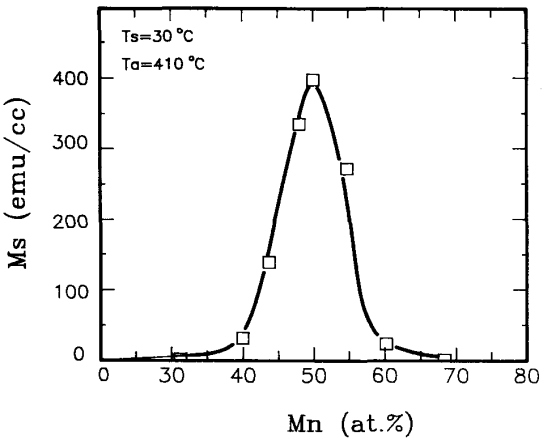

Fig. 1. Variation of saturation magnetization Ms with Mn content.

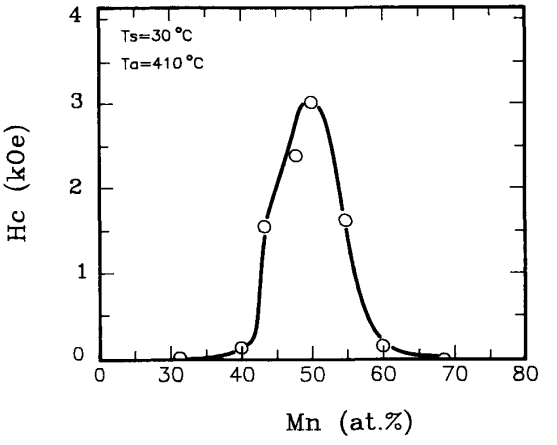

Fig. 2. Variation of coercivity Hc with Mn content.

the relation between Ms and Mn content of these films. The ferromagnetic phase appeared at composition range between 40 to 60 at.%, and the maximum Ms about 400 emu/cc was obtained for the Mn_{50}-Al_{50} films, which was close to that of the τ-phase in bulk Mn-Al alloys [2]. This indicated that the film was almost completely transformed into τ-phase. Fig. 2 shows the relation between the coercivity Hc and the Mn content of the films, the Hc of the Mn_{50}-Al_{50} film was about 3000 Oe, which is much larger than that of the bulk Mn-Al alloys (about 500 ~ 1000 Oe) [2].

Fig. 3 shows the substrate temperature dependence of Ms for the Mn_{50}-Al_{50} films. The as-deposited samples were non-magnetic phase for Ts below 100°C, above which a low Ms value were detected. This indicated that only a small amount of τ-phase formed in the as-deposited films. After annealing these films at 410°C, the Ms increased for all the samples, especially for the films deposited at low Ts. Thus, the $\epsilon \rightarrow \tau$ phase transformation was occurred during the annealing treatment. However, since the Ms of the annealed films decreased with increasing Ts, the transformation fraction should decrease with increasing Ts. The results of x-ray diffraction measurements for the samples of Mn_{50}-Al_{50} films deposited at different substrate temperature are shown in Fig. 4. The intensity of the ϵ-phase peaks increased with decreasing substrate temperature and the half-width of the peaks B decreased with decreasing substrate temperature. This indicates that the films deposited at lower Ts have a large and more perfect crystalline structure than the films deposited at higher Ts. Since the c plane of the hexagonal structure in the ϵ-phase and the (111) plane of the tetragonal structure in the τ-phase have the same spacing distance [3], the results of x-ray diffraction could not identify which phase was formed. Because the ϵ-phase and τ-phase are antiferromagnetic and ferromagnetic, respectively, the results of the Ms measurement (Fig. 3) can confirm that all the as-deposited films are mostly composed of the ϵ-phase.

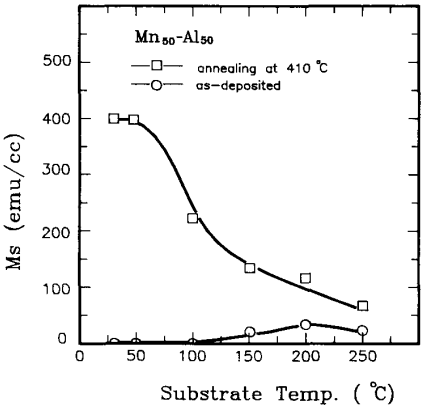

Fig. 3. Saturation magnetization Ms of Mn_{50}-Al_{50} films as a function of substrate temperature. The annealing time is 30 min.

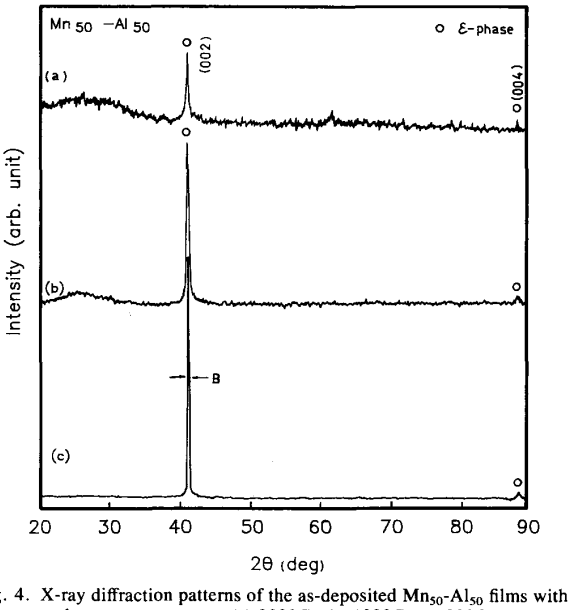

Fig. 4. X-ray diffraction patterns of the as-deposited Mn_{50}-Al_{50} films with substrate temperature: (a) 200°C; (b) 100°C; (c) 30°C.

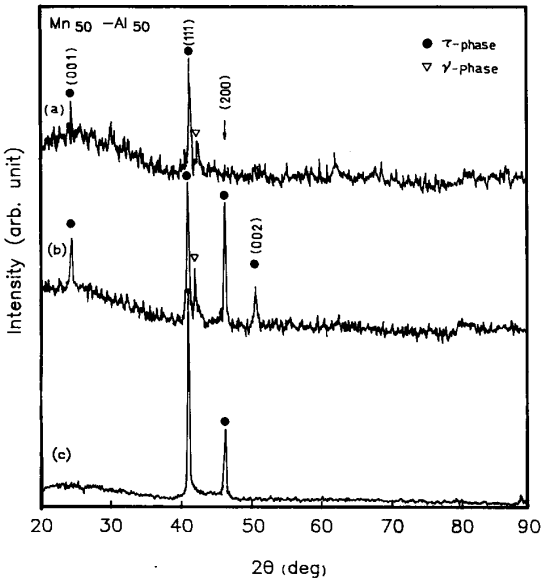

Fig. 5. X-ray diffraction patterns of the corresponding samples in Fig. 4 after annealing at 410°C for 30 min.

The above results indicate that at low substrate temperature the sputtered atoms arrived on the substrate should not have enough energy to form the metastable τ-phase or the equilibrium β and γ-phase, and the ϵ-phases were formed due to the super quenching effect.

After annealing at 410°C for 30 min., the ϵ-phases transfer into τ-phases, their x-ray diffraction patterns are shown in Fig. 5. The annealed samples with Ts above 100°C were composed of γ-phase and τ-phase while the films deposited at Ts of 30°C were composed of pure τ-phases. These results were consistent with the Ms measurement of Fig. 3 which shows that the Ms of annealed films has a maximum value at Ts of 30°C and decreased with increasing Ts. The decrease of Ms is due to that the nonmagnetic γ-phase appeared after the annealing treatment.

In Fig. 5, the diffraction peak of (001) plane (d = 3.54 Å) of the τ-phase was clearly seen in the patterns(a) and (b). It is larger than that of the powder x-ray diffractometry of τ-phase [3], suggesting a preferential orientation of the (001) plane of the τ-phase parallel to the film plane for the two samples. Hence the c axis, which is the easy axis of the τ-phase, is perpendicular to the film plane; this effect was not clear on the M-H loop due to the poor magnetic properties of these films. On the contrary, the films deposited at low Ts of 30°C have a (111) plane of τ-phase crystallites oriented parallel to the film plane. This indicates that the c axis of the τ-phase is incline to the film surface at angle about 37.9° [12].

Fig. 6 shows M-H curves of Mn_{50}-Al_{50} films with Ts = 30°C, the applied fields were in both directions parallel and normal to the film plane. The M-H curves show that the film exhibits almost isotropic characteristics. This consistent with the result of the X-ray diffraction (Fig. 5, pattern (c)) which shows that the (111) plane of τ-phase crystallites parallel to the film plane and the easy crystal axis of the τ-phase incline to the film surface at angle about 37.9°.

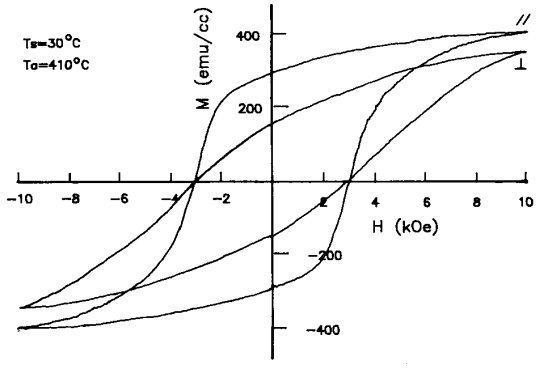

Fig. 6. Magnetization curves for Mn_{50}-Al_{50} films with substrate temperature of 30°C. The annealing time is 30 min.

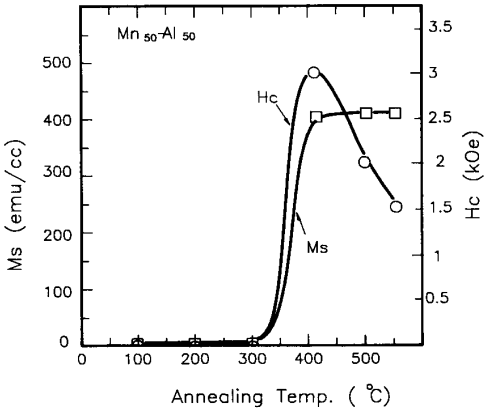

Fig. 7. Annealing temperature dependence on Ms and Hc for Mn_{50}-Al_{50} films. The annealing time is 30 min.

Different annealing temperatures were performed for the Mn-Al films. Fig. 7 shows the magnetic properties of the Mn_{50}-Al_{50} film as a function of annealing temperature between 100 and 550°C. It is seen that the Ms = 0 at annealing temperature below 300°C above which the Ms increased rapidly with increasing annealing temperature and at 500°C, the Ms reached its maximum value and remained unchanged with the temperature. This means that the transformation of ϵ to τ-phase was complete at temperature above 500°C. The Hc decreases with increasing annealing temperature at temperature above 410°C. This may be due to the grain growth at high temperature annealing. However, the exact mechanism is not clear at present. Further research is underway, and will be reported later. The effect of annealing time on the magnetic properties of the Mn_{50}-Al_{50} films was shown in Fig. 8. The Ms was increased rapidly at annealing time above 3 minutes. At the annealing time of about 100 minutes, Ms reached its maximum value of about 420 emu/cc and did not drop even at the annealing time up to 3.5 hours.

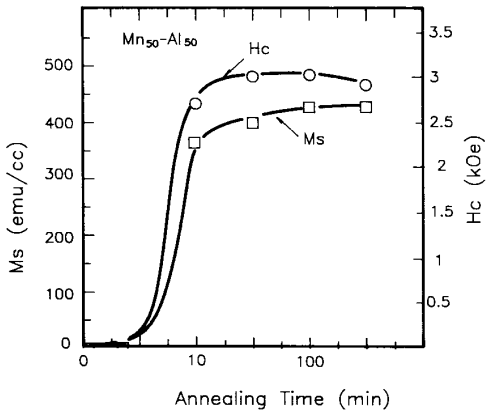

Fig. 8. Annealing time dependence on Ms and Hc for Mn_{50}-Al_{50} films. The annealing temperature is 410°C.

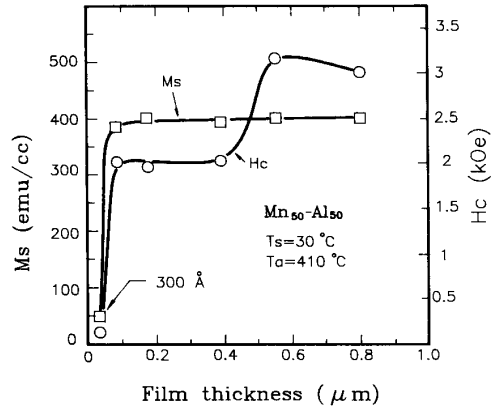

Fig. 9. Thickness dependence on Ms and Hc for Mn_{50}-Al_{50} films. The annealing time is 30 min.

From the above results, it is found that the Mn_{50}-Al_{50} films have a very high thermal stability. This is in contrast to the work of Morisako *et al.* [14], who found that the τ-phase in the Mn_{60}-Al_{40} and Mn_{57}-Al_{40}-Ni_3 decomposed into equilibrium phase and Ms decrease rapidly at temperature above 400°C. The τ-phase of our Mn_{50}-Al_{50} films were stable even elevating the annealing temperature up to 550°C.

Fig. 9 shows the thickness dependence of Mn_{50}-Al_{50} films on the magnetic properties. For the decrease of film thickness to about 1000 Å, the Ms decreased slightly with decreasing film thickness. Below 700 Å, the Ms decreased rapidly to about 50 emu/cc for the 300 Å film. Since the formation of the ferromagnetic τ-phase is a shear transformation [9], the transformation occurred by cooperative atomic movements. Atoms in the interface region between the substrate and the Mn-Al film were hardly expected to take place during the shear transformation because the movements of these atoms were restricted by the rigid substrates. This effect may hamper the $\epsilon \rightarrow \tau$ transformation especially in the ultra thin film and leads to the sharp decrease of Ms.

The Hc of the films with thickness between 700 Å and 0.4 μm was about 1900 Oe, and it increased to a maximum value of about 3200 Oe at film thickness of 0.58 μm. The coercivity of these Mn-Al films was large than that of the bulk Mn-Al alloys (500 ~ 1000 Oe). This is due to that the magnetoelastic energy arises from the rather high stress between substrates and Mn-Al films during the shear transformation. The internal stresses in the Mn-Al films presumably have a maximum value at the film thickness of about 0.58 μm.

IV. Conclusion

We have studied the sputtered thin films of the Mn-Al system over a wide composition range and for various substrate temperatures. A ferromagnetic τ-phase of Mn_{50}-Al_{50} films with high Ms and Hc have been produced, they have a high coercivity up to about 3000 Oe and a large saturation magnetization of about 420 emu/cc.

The films deposited at low substrate temperature (30°C) were composed of ϵ-phase with well crystallite structure, and they will transfer into τ-phases after annealing at temperature about 410°C. Increasing the substrate temperature will decrease the crystallite size of the as-deposited film, and the nucleation of equilibrium γ-phase occurred as well. Thus, a single τ-phase cannot be obtained by further annealing treatment.

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