Magnetic properties and microstructure of Mn–Al–C thin films

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$Mn_xAl_{100-x-y}C_y$ thin films with $x=35-65$ at. % and $y=0-2.4$ at. % were prepared by rf magnetron sputtering. Effects of the chemical composition and annealing temperature on the magnetic properties and microstructure of Mn–Al–C films were investigated. X-ray analysis shows that the as-deposited Mn–Al–C thin films are amorphous, and their saturation magnetization is very low. After annealing at temperatures between 400 and 550 °C in vacuum for 30 min, the magnetic phase with higher carbon concentration shows better thermal stability. The best annealing condition was found to be at 410 °C for 30 min. A ferromagnetic τ phase with a grain size of roughly 200–250 nm appeared at a composition range between 40 and 60 at. % Mn for $Mn_xAl_{99-x}C_1$ thin films; and the sample with $Mn_{50}Al_{49}C_1$ has high coercivity and moderate saturation magnetization. The carbon addition can increase the thermal stability of the coercivity of the Mn–Al thin films. © *1999 American Institute of Physics.* [S0021-8979(99)60308-5]

I. INTRODUCTION

Magnetic properties of Mn–Al thin films have been extensively studied by the rf magnetron sputtering[1–5] and by molecular beam epitaxy (MBE) techniques.[6,7] The stabilization of the metastable τ phase in the bulk Mn–Al alloy system was first described by Kono[8] in 1958 and Koch *et al.*[9] In 1960, they prepared a Mn–Al τ phase by controlled cooling of a high-temperature ϵ phase. The magnetic τ phase has a tetragonal $L1_0$-type superstructure and a high magnetocrystalline anisotropy constant as large as about 10^7 erg/cc. The magnetic moment is carried by the Mn atoms and points along the *c* axis which is, therefore, the magnetic easy axis. The Mn atoms within a Mn sublattice are coupled ferromagnetically, however, the moments of the Mn atoms in the Al sublattice sites are in the opposite direction.[10] The bulk Mn–Al alloy with the τ phase has a coercivity of $H_c = 500-1000$ Oe.

The Mn–Al thin films with a τ phase can be used in: (1) novel semiconductor devices based on the spatially modulated magnetic field or on the injection and detection of spins,[11] (2) generation of a bias field (e.g., in magnetic-field sensors) through magnetostatic fields or the exchange interaction,[12] (3) magnetic and magneto-optic recording,[2–5] and (4) nonvolatile memories.[7]

For a bulk alloy, the τ phase is formed by cooling the high-temperature nonmagnetic ϵ phase (hcp) followed by heat treatment at 450–600 °C.[13] Recent studies of electron microscopy observations and kinetic analysis provide evidence that the $\epsilon \rightarrow \tau$ transformation may involve a diffusion, nucleation, and growth process.[14] In this study, a nonmagnetic ϵ-phase thin film was formed preliminarily by magnetron sputtering and a magnetic τ phase is obtained by heat treatment around 400 °C for pure Mn–Al films.

In this work, we study the effect of carbon doping on the stabilization of the magnetic phase and microstructure of the Mn–Al films.

II. EXPERIMENT

Mn–Al–C films were fabricated by means of a rf magnetron sputtering system. High-purity aluminum (99.999%), manganese (99.99%), and graphite were melted in a graphite crucible at a temperature around 1400 °C. The ingot was cut into 2 mm thickness and polished as a sputtering target. The base pressure in the system was 5×10^{-7} Torr, and the Ar sputtering pressure was kept at 1 mTorr. The sputtering rate was 0.5 nm/s. Films with thickness of 0.8 μm were used in this study. Thermal annealing was carried out at a temperature range between 350 and 550 °C in vacuum and the annealing time was 30 min.

The crystal structures and microstructure of the as-deposited and annealed films were characterized by x-ray diffractometer (XRD) and transmission electronic microscope (TEM). Compositions of the films were determined by an electron probe microanalyzer (EPMA) calibrated by a standard $Mn_{55}Al_{45}$ alloy. The magnetic properties of the films were measured with a vibrating sample magnetometer (VSM) at room temperature with a maximum applied field of 20 kOe and the applied field is parallel to the film plane.

III. RESULTS AND DISCUSSION

The x-ray diffraction patterns of (a) the as-deposited $Mn_{50}Al_{49}C_1$ film and (b) the pure Mn–Al film are shown in Fig. 1. It shows a crystalline ϵ phase in the $Mn_{50}Al_{50}$ film and an amorphous state in the as-deposited $Mn_{50}Al_{49}C_1$ film. The amorphous structure is a nonmagnetic phase. Figure 2

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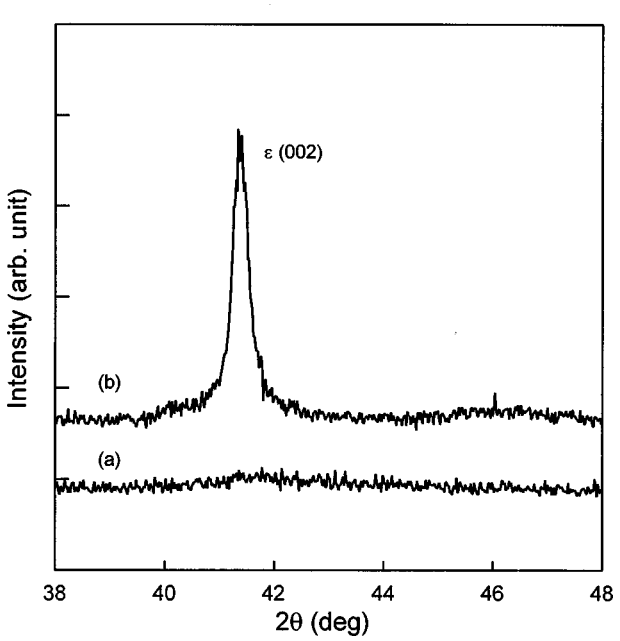

FIG. 1. X-ray diffraction patterns of the as-deposited films: (a) $Mn_{50}Al_{49}C_1$; and (b) $Mn_{50}Al_{50}$.

shows the saturation magnetization M_s and coercivity H_c of the MnAlC films with annealing at 410 °C for 30 min. The optimum manganese content is found to be about 50 at. %. Figure 3 shows the M_s and H_c values of the $Mn_{50}Al_{49}C_1$ film as functions of annealed temperatures between 200 and 600 °C. Both M_s and H_c increase rapidly with increasing annealing temperature up to 400 °C due to the formation of the magnetic τ phase. Above 400 °C they decrease with increasing annealing temperature due to the nonmagnetic phases precipitated at high temperature. From the x-ray diffraction pattern study of the annealed films with various thickness, it is found that when the film thickness is less than 200 nm, the magnetic τ phase is difficult to form. Since the formation of the ferromagnetic τ phase is a shear transformation, the transformation occurs by cooperative atomic movements. Atoms in the interface region between the substrate and the Mn–Al–C film were hardly expected to move during the shear transformation because the movements of these atoms were restricted by the rigid substrates. This effect[15] may hamper the τ-phase formation, especially in the ultrathin films, and lead to the sharp decrease of M_s. H_c of these Mn–Al–C films is larger than that of the bulk Mn–Al–C alloys. This is due to the magnetoelastic energy arising from the rather high stress between the substrates and Mn–Al–C films during the shear transformation.

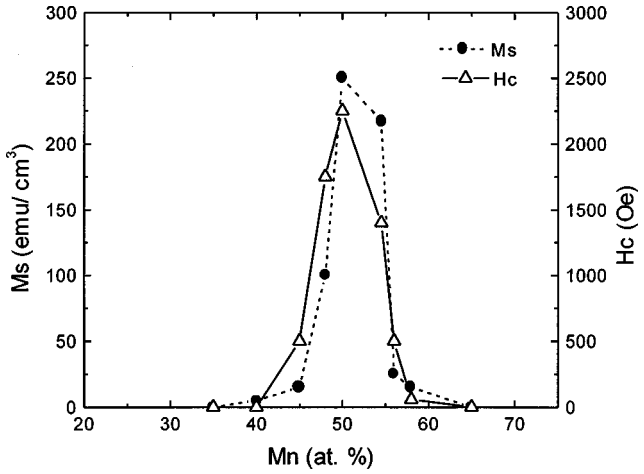

FIG. 2. (a) M_s and (b) H_c as functions of Mn content for the Mn–Al–C film with 1.0 at. %C.

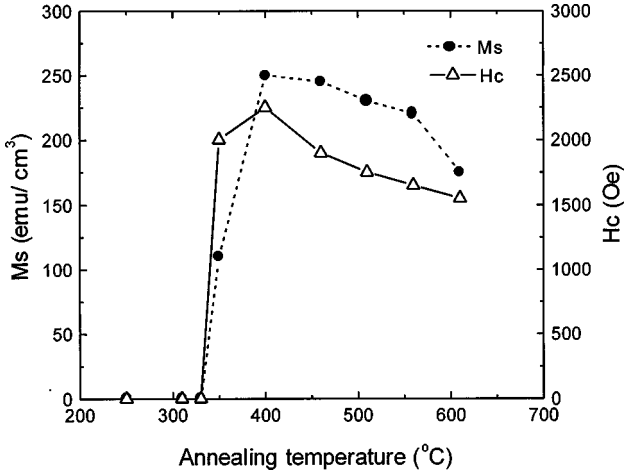

FIG. 3. (a) M_s and (b) H_c as functions of annealing temperature for the $Mn_{50}Al_{49}C_1$ film.

Figures 4(a) and 5(a) show the TEM microstructure of the $Mn_{50}Al_{49}C_1$ film for the as-deposited and annealed at

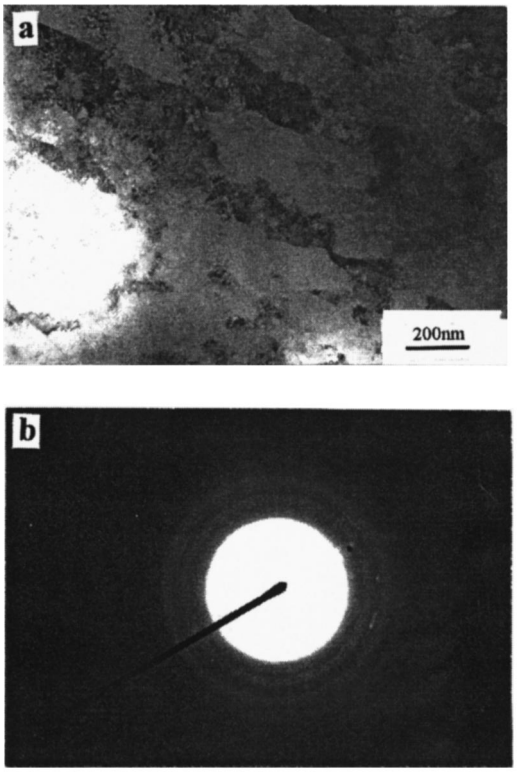

FIG. 4. TEM analysis of the as-deposited $Mn_{50}Al_{49}C_1$ film: (a) microstructure; and (b) SAD pattern.

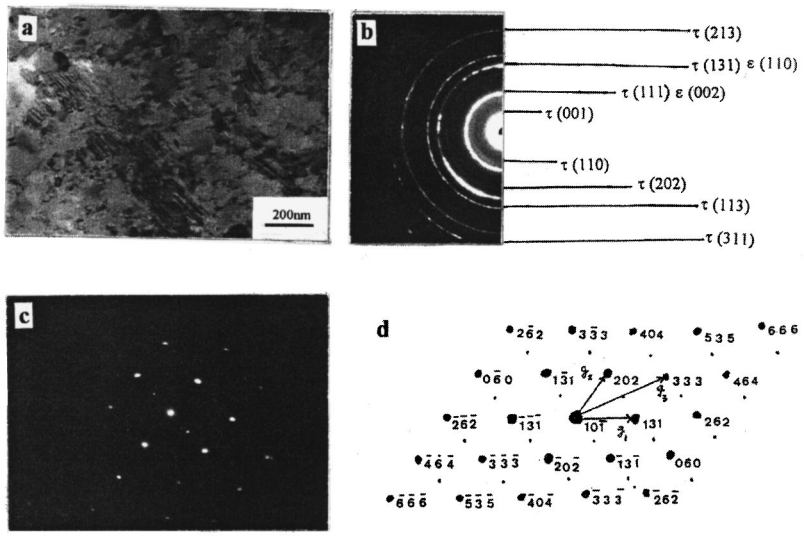

FIG. 5. TEM analysis of the $Mn_{50}Al_{49}C_1$ film annealed at 410 °C: (a) microstructure; (b) SAD pattern; (c) spot pattern of a τ-phase crystal; and (d) indices of the spot pattern.

410 °C samples, respectively. The selective area diffraction (SAD) pattern in Fig. 4(b) is a typical pattern of an amorphous structure, and in Fig. 5(b) shows the τ phase is the major phase. The τ phase has a plate structure with an average crystal size around 200–250 nm, as shown in Fig. 5(a). Spots diffraction analysis of this τ-phase crystal is presented in Fig. 5(c). These spots have been analyzed and their indices are shown in Fig. 5(d).

The temperature coefficient of the coercivity, defined by dH_c/dT, is determined between 20 and 100 °C. The values of dH_c/dT for the $Mn_{50}Al_{50-y}C_y$ films as a function of the C concentration of y are shown in Fig. 6. The value of dH_c/dT of the film decreases from -13 to -2 Oe/°C by increasing the C concentration of y from 0.0 to 2.0. There is a large difference in the atomic radius between the Mn(1.31 Å), Al(1.43 Å), and metalloid C(0.77 Å), it is expected that the C atoms would be dissolved in the τ phase interstitially.[16] However, the reason for the decrease of dH_c/dT with increasing C content is still not clear. Further investigations are undertaken and will be reported later.

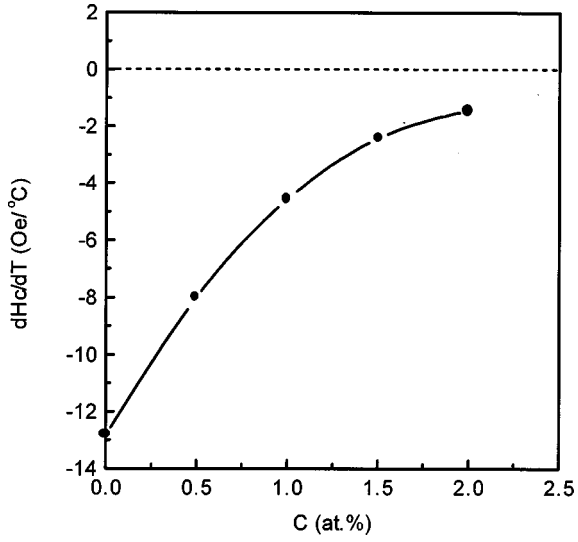

FIG. 6. Temperature-dependent coefficient of coercivity dH_c/dT as a function of carbon content for the $Mn_{50}Al_{50-x}C_x$ thin film.

In conclusion, we have studied the magnetic properties and microstructure of Mn–Al–C thin films over a wide composition range. The carbon addition causes an amorphous structure, which is formed at the sputtering process. An annealing treatment between 400 and 550 °C transfers the amorphous structure into the magnetic τ-phase structure. Carbon addition can increase the thermal stability of the coercivity of Mn–Al thin films.

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