Effects of thin MnAl buffer layer on structural and magnetic properties of MnAl films*

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Thin Mn(2 nm)/Al(2 nm) bilayers serving as buffer layers have been prepared prior to the deposition of MnAl films. The ferromagnetic τ-phase forms in the buffer layers at an optimum substrate temperature. As a template it induces the growth of following MnAl film. Compared with the case of film without buffer layer, the growth of non-ferromagnetic phase is suppressed and the structural and magnetic properties of MnAl film are improved. Weak dipolar inter-grain coupling is revealed in the MnAl film, and the magnetic reversal process is dominated by magnetic moment rotation.

Keywords: $L1_0$, τ–MnAl, buffer layer

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1. Introduction

MnAl alloy film with the ferromagnetic τ-phase (tetragonal $L1_0$-type superstructure) is a candidate in magnetic devices or data storage systems, because of its large magneto-crystalline anisotropy ($K_\mu = 1.7 \times 10^7$ erg/cm^3) and coercivity.[1,2] The ferromagnetic τ–MnAl films have been prepared previously in bulk by quenching, in powder by mechanical milling (MM), and in film by molecular beam epitaxy (MBE), pulsed laser deposition (PLD) and DC magnetron sputtering.[3−11] Though sputtering is a widely-used method for film preparation, pure τ–MnAl is difficult to obtain in sputtered films.[8−11] According to phase diagram, τ phase only forms at a narrow composition range: Mn content 50–60 at%.[8,9] Composition variation in the sputtered films is expected to induce the formation of non-ferromagnetic phases.[12] Next, a phase transformation which is ε(A3) $\rightarrow$ ε'(B19) $\rightarrow$ $\tau(L1_0)$ is necessary to approach the ferromagnetic phase since ε phase always forms in the as-deposited film prepared at room temperature.[8−11] Post-annealing or substrate heating is required. However, the temperature window is limited,[8,13] because τ–MnAl which is metastable will decompose into β–Mn and γ_2–MnAl at high temperatures. Moreover, the window decreases with the increase of film thickness. Finally, sputtering is similar to an ultrafast quenching process and hard to achieve a homogeneous film structure just as that of epitaxial film. Therefore, mixed phases are usually obtained in the sputtered films.

Considering the narrow growth window of τ–MnAl films, Sands *et al.*[5] and Harbison *et al.*[13] suggested a two-step method. Before the epitaxial growth of τ–MnAl films, a thin buffer layer acting as the nucleation points was developed. The buffer was so thin that the $L1_0$ superstructure could be obtained readily. The tetragonal structure was followed in the coming deposition.[14] High quality single crystal τ–MnAl film was obtained. In order to improve the structural and the magnetic properties of MnAl films, the influence of a thin MnAl buffer layer is investigated in this paper.

2. Experiment

The MnAl films were prepared in a conventional DC magnetron sputtering system (Lesker CMS-18) as described in Ref. [11]. Mn/Al bilayers with 2-nm Mn and 2-nm Al serving as the buffer layer were deposited on glass substrates at different substrate temperatures ranging from 150 °C to 300 °C, which was maintained for 30 min before buffer layer deposition. After the substrate temperature decreased to room temperature, $[Mn/Al]_{15}$ multilayers were deposited on the

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buffer layer. Multilayer structure was the same as that of our previous samples, i.e., the periodic thickness of each Mn/Al bilayer was 4 nm and the total thickness of the films was 64 nm. Thermal annealing of $[Mn/Al]_1/[Mn/Al]_{15}$ films was carried out in a temperature range between 300 °C and 500 °C in vacuum better than -4×10^{-4} Pa. The typical annealing duration was 30 min. Magnetic properties were measured by a vibrating sample magnetometer (VSM) and magneto-optical Kerr effect equipment (MOKE). Both isothermal remanence magnetization curve (IRM) and demagnetizing remanence magnetization curve (DCD) were measured by VSM in order to analyse the interaction between the magnetic grains. The microstructure of the films was characterized by x-ray diffractometer (XRD) with the x-ray wavelength 0.15418 nm.

3. Results and discussion

Multilayers deposition followed by annealing is a convenient way to prepare the $L1_0$ MnAl alloy films with alternative arrangement of Mn and Al layers.[11] However, nonferromagnetic phases, such as β–Mn and/or γ–MnAl (or ε–MnAl), are accompanied with the formation of τ–MnAl. The effect of the buffer layer is to provide a template inducing the τ-phase MnAl. Figure 1 shows the dependences of XRD θ–2θ scans of MnAl films on substrate temperatures of buffer layer deposition. All the samples were annealed at 400 °C for 30 min the same as that in Ref. [11]. The growth of nonferromagnetic phase whose peak appears at about 42.3° is suppressed, and only τ–MnAl is revealed by x-ray diffraction. Thus, the buffer layer is favourable for τ–MnAl nucleation and growth. Nevertheless, the (101) peak is broader than our previously obtained one, which implies that the MnAl films with buffer layers have small grain sizes. In addition, the intensity of MnAl (101) peak becomes weak with the increase of substrate temperature for buffer layer.

With the increase of the substrate temperature for buffer layers as shown in Fig. 2(a), the saturation magnetization of MnAl film increases first, reaching the maximum at 230 °C and then decreases. The maximum $M_S = 135$ emu/cc is approximately doubled compared with that of MnAl film without buffer layer in our previous experiment.[11] Both in-plane (IP) and out-of-plane (OP) coercivities firstly decrease with the increase of substrate temperature of buffer layer, and then increase. The results are assumed to be due to the phase variations of the MnAl buffer layers, which depend on the preparation temperature.[8,13] By heating the substrate, Mn, Al atoms are readily to move on the substrate[13] and their mobility increases with the substrate temperature. Besides, the buffer is so thin that the uniform film structure may be suggested. Hence, crystalline τ-phase can form in the buffer layer at an optimum temperature. Then the consequent deposition atoms can follow the template, and the growth of τ–MnAl becomes possible. As temperature further increases, however, other equilibrium phases, such as γ–MnAl and β–Mn, should form. Once they nucleate, they dominate the subsequent MnAl film growth and ferromagnetic properties are destroyed. Hence, the M_S peak implies that 230 °C is the optimum temperature for τ-phase formation in the buffer layer. In addition, the hysteresis loops shown in Fig. 3 indicate that the easy axis tends to be in the in-plane direction.

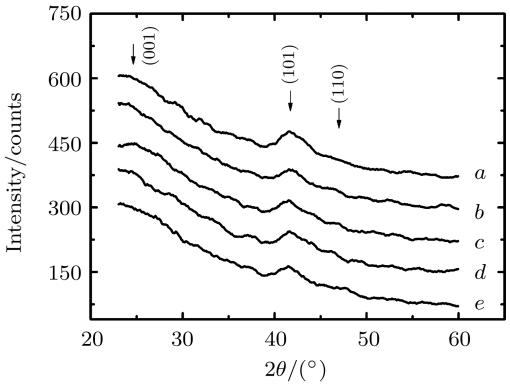


Fig. 1. XRD θ–2θ scans of MnAl films with Mn/Al bilayer buffers. The buffer layers are grown at 150 (curve *a*), 190 (curve *b*), 230 (curve *c*), 270 (curve *d*), and 300 °C (curve *e*). All the samples were post-annealed at 400 °C for 30 min.

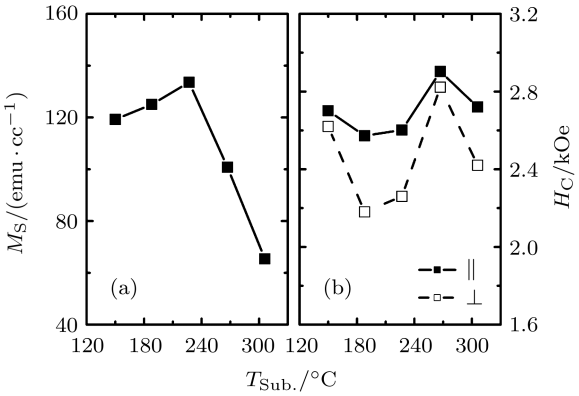


Fig. 2. Dependences of magnetic properties (saturation magnetization M_S (a) and coercivity H_C (b)) on substrate temperature, with samples annealed at 400 °C for 30 min, 1 Oe = 80 A/m.

The influence of annealing temperature on magnetic properties was studied by VSM, on the samples

of which the buffer layers were deposited at 230 °C. As indicated in Fig. 4, saturation magnetization M_S and coercivity H_C show a similar tendency to those of MnAl films without buffer layers.[11] Very small ferromagnetic phase is found when annealing temperature is lower than 350 °C. With further increase of annealing temperature, the highest values of M_S and H_C emerge after sample annealing at 400 °C. And then, both the magnetization and the coercivity decrease. However, M_S nearly doubles compared with that of MnAl film without buffer layer. The τ–MnAl buffer layer is favourable for obtaining ferromagnetic phase.

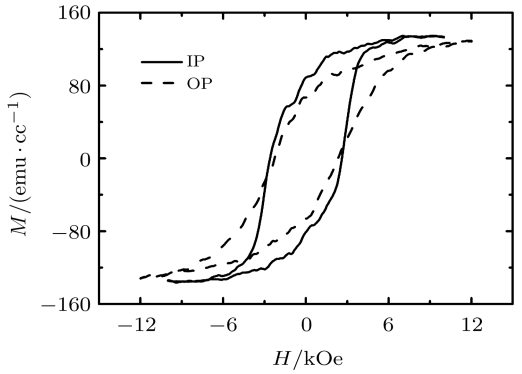


Fig. 3. In-plane (IP) and out-of-plane (OP) hysteresis loops of MnAl samples annealed at 400 °C for 30 min, with the buffer layer prepared at 230 °C.

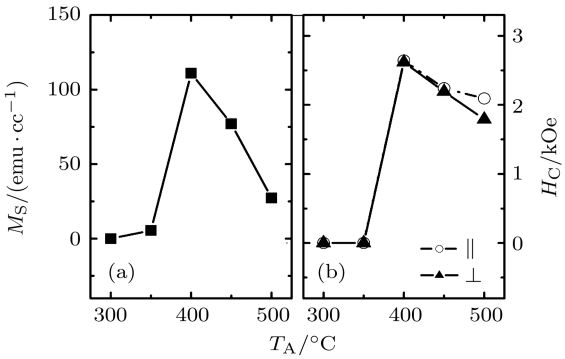


Fig. 4. Dependences of magnetic properties (saturation magnetization M_s (a) and coercivity H_C (b)) of MnAl films on annealing temperature, with the Mn/Al buffer layers of all the samples deposited at 230 °C.

Furthermore, we study the influence of annealing duration on the magnetic properties of the MnAl films (Fig. 5). All the samples are annealed at 400 °C. Both the saturation magnetization and the in-plane coercivity decrease with the duration. By extending the duration Mn and Al atoms have longer time to move and more energies to crystallize. The nonferromagnetic equilibrium phases, such as γ–MnAl and β–Mn are readily to form. Hence, the magnetic properties are degraded with the increase of annealing time. Moreover, a similar tendency is seen in the three series samples. It confirms the effect that a suitable buffer layer works on the formation of the ferromagnetic τ–MnAl.

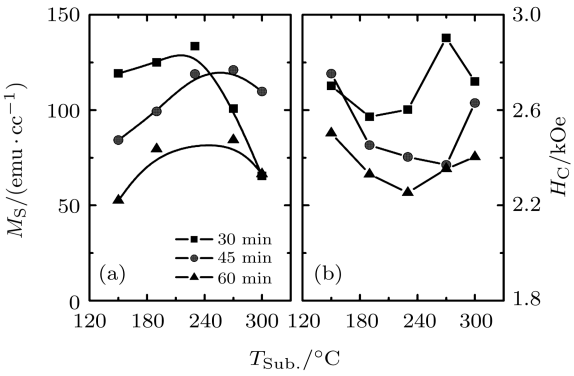


Fig. 5. Dependences of magnetic properties (saturation magnetization M_s (a) and in-plane coercivity H_C (b)) of MnAl films annealed at 400 °C for different annealing durations, where full square, circle and triangle correspond to 30, 45 and 60 min annealing, respectively.

In order to evaluate the inter-grain interaction in the MnAl films, $\Delta M(H)$ curve, defined as $(m_{DCD}(H) - [1 - 2m_{IRM}(H)])$ $(m = M/M_R)$, was introduced.[15,16] Also, the energy barrier distributions for magnetization reversal were obtained from the first differential of the DCD and IRM curves to understand the reversal mechanism.[15] For the sample shown in Fig. 6, no sharp changes appear in the IRM curve and the DCD curve along the in-plane direction. The small negative $\Delta M(H)$ peak shows that the interaction between grains is mainly dipolar coupling which attempts to demagnetize the film, and its intensity is weak. Moreover, the peaks of two energy barrier distributions are at the same point (Fig. 6(b)). The results indicate that the magnetic reversal process is dominated by magnetic moment rotation. A similar reversal mechanism is obtained in other films deposited on different buffer layers.

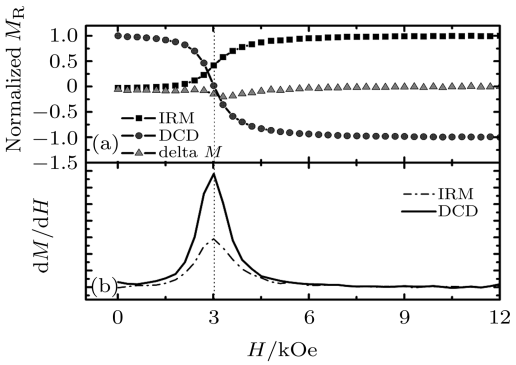


Fig. 6. (a) IRM, DCD remanence and delta M ($\Delta M(H)$) curves of 400 °C annealed MnAl sample of which buffer layer was prepared at 230 °C, and (b) the first differentials of DCD remanence and IRM curves.

4. Conclusion

The effects of buffer layer on the structural and the magnetic properties of MnAl films were investigated. The Mn/Al bilayer buffer is thin (4 nm) so that the required temperature for the formation of τ–MnAl is easy to approach because of the uniform film structure. The ferromagnetic τ-phase then is readily to form in the buffer layer at an optimum substrate temperature. Following the template, the growth of non-ferromagnetic phase is suppressed, and only τ–MnAl is revealed by XRD. Thus, the structural and the magnetic properties of MnAl films are improved. Besides, the IRM, DCD and ΔM curves are measured. Weak dipolar inter-grain coupling is revealed in the MnAl films by the ΔM curve. The magnetic reversal process is dominated by magnetic moment rotation for all the samples. The maximum saturation magnetization $M_{\rm S} = 135$ emu/cc, is obtained in the sample $[\mathrm{Mn}(2\ \mathrm{nm})/\mathrm{Al}(2\ \mathrm{nm})]_{15}$ annealed at 400 °C for 30 min, with the buffer layer Mn(2 nm)/Al(2 nm) prepared at 230 °C.

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