Epitaxial growth of $Co_2Cr_{0.6}Fe_{0.4}Al$ Heusler alloy thin films on MgO (001) substrates by magnetron sputtering

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Abstract

We demonstrate that single-crystalline epitaxial films of the Heusler alloy $Co_2Cr_{0.6}Fe_{0.4}Al$ (CCFA) featuring excellent surface flatness can be grown on MgO (001) substrates by magnetron sputtering deposition at room temperature and subsequent annealing at high temperatures. X-ray pole figure measurements reveal that the films exhibit the B2-type structure and the [100] direction of the films is rotated by 45° from the [100] direction of the MgO substrate. Moreover, their Curie temperatures and saturation magnetizations are also improved by annealing. The surface roughness is about 0.2 nm rms according to atomic force microscopy.

Key words: A3. Physical vapor deposition processes; B2. Magnetic materials; Heusler alloys

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1 Introduction

There has been growing interest in the field of spintronics[1], which involves exploration of the extra degree of freedom provided by electron spin with a view to realizing new functionalities in future electronic devices. One key to making such a spin device is to utilize the ability of ferromagnetic metals to conduct spin-polarized current. The effectiveness of magneto-electronics, therefore, depends on how much a current is spin-polarized. In this context, materials with a large spin-polarization are favorable for spintronic devices.

Heusler compounds[2,3] have received considerable attention because they have been predicted to exhibit half-metal ferromagnetic (HMF) behavior, which is characterized by the coexistence of metallic behavior for one electron spin and insulating behavior for the other. Thus, the electronic density of states is completely spin polarized at the Fermi level. Cobalt-based full-Heusler alloys have been considered potential candidates for showing HMF properties. Their structural and magnetic properties have been intensively investigated experimentally[4–18] and theoretically[19–23] because they have comparatively high Curie temperatures T_{C}. In particular, $Co_2Cr_{1-x}Fe_xAl$ (CCFA) is expected to have suitable electro-magnetic properties for injecting a spin-polarized current[16,22].

In most studies of the fabrication of Co-based Heusler alloy thin films, materials have been deposited by sputtering using a high substrate temperature and metallic seed-layers to stabilize the proper crystal structure[4,5]. For practical use in heterostructures, however, the existence of seed-layers will give rise to

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more complicated fabrication procedures. Besides, a high substrate temperature during deposition will be detrimental to the smooth interface required for spintronic devices[24]. Therefore, it is essential to fabricate epitaxial, single-crystalline thin films of CCFA directly on substrates and to characterize their structural and magnetic properties.

In this paper, we report on the preparation and characterization of epitaxial, single-crystalline CCFA thin films grown by rf-magnetron sputtering directly on MgO (001) substrates. Unlike the existing CCFA thin films, our thin films were deposited at room temperature and subsequently annealed at high temperatures. This method greatly improved their crystal structures and magnetic moments. Moreover, the surface roughness of our films is fairly small, typically 0.2 nm rms or less. Thus, CCFA films obtained in this study are suitable as a key element of heterostructures in spintronic devices.

2 Experimental

Heusler alloys are ternary inter-metallic compounds with the composition X_2YZ in $L2_1$ (space group: $Fm\bar{3}m$) cubic structure. A typical Heusler alloy consists of two different transition metals X and Y and a non-magnetic element Z as shown in Fig. 1(a). Since the lattice mismatch between CCFA (a_{CCFA} ∼5.737Å[18]) and diagonal length of MgO ($\sqrt{2} \times a_{MgO} = 5.954$Å) is relatively small ($\sim 3\%$) as shown in Fig. 1(b), it is reasonable to expect that the CCFA films will grow epitaxially with their [100] direction rotated by 45 $^\circ$ from the MgO [100] direction.

The CCFA films grown in this study were deposited by rf-magnetron sputtering on MgO (001) substrates at room temperature. High-purity Ar was used as the sputtering gas at a pressure of 0.1 Pa and the base pressure of our system was $\sim 5 \times 10^{-6}$ Pa. The CCFA target used in this study was a commercially provided stoichiometric ingot with a 2-inch diameter and the sputtering rate was 0.05 nm/s. After deposition, the films were annealed at high temperatures. The film structures were investigated by performing X-ray Bragg scans and X-ray pole figure measurements (Bruker AXS D8 DISCOVER). The surface morphologies were observed by atomic force microscopy (Digital Instruments). Magnetic properties were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS).

3 Results and discussion

3.1 Structural properties

An X-ray Bragg scan of 100-nm-thick CCFA films grown on MgO (001) is shown in Fig. 2. Clear (200) and (400) peaks of CCFA were observed in the annealed films whereas these peaks were not observed in the as-deposited films. Moreover, the intensity of the peaks increased with annealing temperature. These results show that the crystal structure of CCFA film was improved by annealing at 500–600°C.

The $L2_1$ structure illustrated in Fig. 1(a) produces Bragg reflections when the Miller indices (hkl) of the scattering planes are either all odd or all even[7]. The reflections from (200) and (111) are superlattice reflections and their structure amplitudes are described as $F(111) = 4|f_{\mathrm{Y}site} - f_{\mathrm{Al}}|$ and $F(200) = 4|2f_{\mathrm{Co}} - (f_{\mathrm{Y}site} + f_{\mathrm{Al}})|$, where f_is are the average scattering factors for each atom site and "Y site" is Cr or Fe. If preferential disorder occurs only between certain sites, then $F(111)$ and $F(200)$ will be affected differently: $F(200)$ is unaffected by preferential (Y site − Al) disorder and is reduced in intensity by the factor S^2, whereas $F(111)$ is reduced by the factor $(1-2\alpha)S^2$, where S and α are the degree of long-range order and the preferential disordering parameter, respectively. When $\alpha = 0.5$, complete disorder exists between the Y site and Al and the structure reduces to the B2-type($Pm\bar{3}m$). Then, the Bragg reflections from the (111) plane vanish while those of (200) can be observed. The reason that (200) and (400) peaks were not observed for the as-deposited film in the X-ray Bragg scan (Fig. 2(a)) may be due to the existence of both structural and atomic disorder in the as-deposited film. Annealing greatly improved the crystal structure. As a result, the (400) peak appeared in the X-ray diffraction pattern and its intensity became larger. Moreover, atomic disorder was also reduced by subsequent annealing, so the (200) peak could be observed. On the other hand, CCFA(111) could not be observed, which implies the existence of complete disorder between the Y site and Al, while Co atoms occupy suitable sites. The appearance of the (200) superlattice line for the annealed films indicates that the films were mostly the B2-type structure but some regions with A2-type structures (amounting to a small total area) might coexist.

To confirm the in-plane structure of CCFA films, X-ray pole figure measurement was performed. A pole figure scan of CCFA film annealed at 500˚C on an MgO substrate is shown in Fig. 3. As can be seen in Fig. 3(a), {111} components of the MgO substrate with fourfold symmetry with respect to the sample rotation angle ϕ were clearly observed at tilt angle χ of 54.7˚. Figure 3(b) also exhibits the fourfold symmetry of the CCFA {220} principal reflection peaks at $\chi = 45^\circ$ and shows that the [100] direction of the CCFA films is rotated by 45° in the ϕ direction from the MgO [100] direction in the (100) plane. These results reveal that the CCFA films deposited on MgO (100) substrates at room temperature and subsequently annealed at high temperatures are epitaxial and single-crystalline films.

In this experiment, we also made CCFA films annealed at higher temperatures (700–900˚C). However, they exhibited many unidentified peaks in both X-ray Bragg scans and X-ray pole figure measurements, implying that films annealed above 700˚C decomposed into other materials.

An AFM image of the surface of 600˚C-annealed CCFA thin film is shown in 4. The scan area is $1\mu\text{m} \times 1\mu\text{m}$. The picture reveals a flat surface morphology with a roughness of about 0.2 nm rms.

3.2 Magnetic Properties

Figure 5 shows the temperature dependence of the magnetization for as-deposited film (△) and 500˚C-annealed film (•). The Curie temperature T_C was estimated by extrapolation to be about 700 K for 500˚C-annealed film and about 500 K for as-deposited film. Moreover, the saturation magnetization M_s was increased by annealing. M_s of 500˚C-annealed film at 10 K was 512 emu/cm^3, which corresponds to a magnetic moment of 2.66 μ_B per formula unit (f.u.).

The magnetic moment calculated using the first-principles calculation method for $Co_2Cr_{0.6}Fe_{0.4}Al$ with the $L2_1$ structure was $\sim 3.8\mu_\mathrm{B}$/f.u.[21,22]. Miura *et al.*[22] have shown theoretically that for Co_2CrAl, the magnetic moment is hardly influenced by the disorder between Cr and Al, which leads to the B2 structure in the fully disordered case. As described above, the 500°C-annealed film mainly consisted of the B2 structure. If we compare the experimentally obtained magnetic moment of 2.66 μ_B/f.u. at 10 K for the 500°C-annealed $Co_2Cr_{0.6}Fe_{0.4}Al$ film with the value calculated for the $L2_1$ structure, the former corresponds to about 70% of the latter. The difference suggests that the 500°C-annealed film does contain some Co-Cr disorder (the A2 type disorder).

Figure 6 shows the magnetic hysteresis curves at room temperature for as-deposited film (△) and 500°C-annealed film(•). All the films showed a small coercive force around 20 Oe and saturation above 100 Oe.

4 Summary

In summary, we have shown that single-crystalline epitaxial $Co_2Cr_{0.6}Fe_{0.4}Al$ (CCFA) Heusler alloy thin films featuring small roughness about 0.2 nm rms can be grown on MgO (001) substrates by magnetron sputtering deposition at room temperature and subsequent annealing at high temperatures. Moreover, their Curie temperature and saturation magnetization are also improved by annealing. These results indicate that CCFA thin films are suitable for application to elements of TMR heterostructures.

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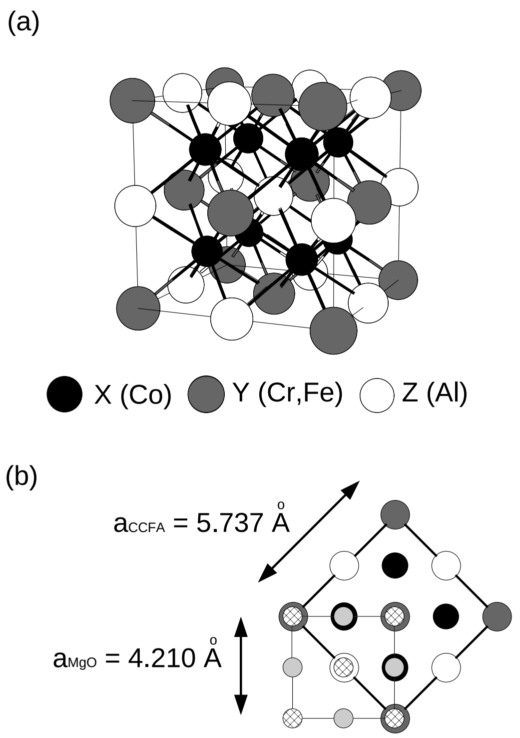

Fig. 1. (a) Schematic view of the $L2_1$ crystal structure with composition X_2YZ. The lattice consists of four different fcc sublattices. Each has an atom basis as follows: X element at (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4), Y at (0, 0, 0) and Z at (1/2, 1/2, 1/2). (b) Top view of CCFA crystal structure. MgO cubic structure is superimposed.

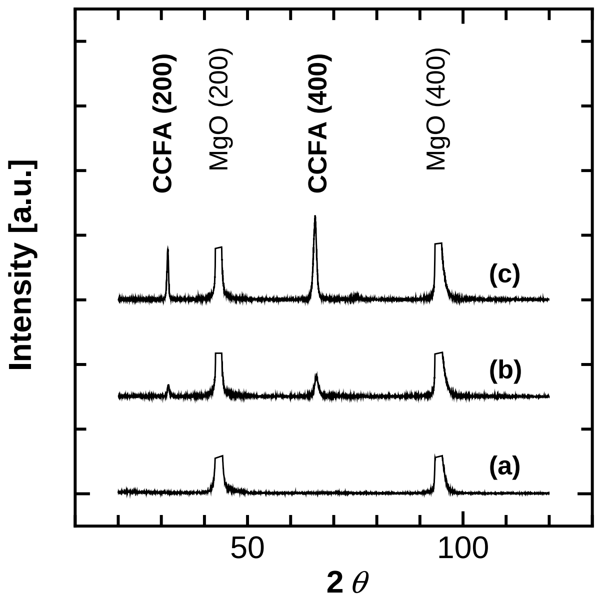

Fig. 2. Typical X-ray diffraction patterns of (a) as-deposited, (b) 500˚C-annealed, and (c) 600˚C-annealed films.

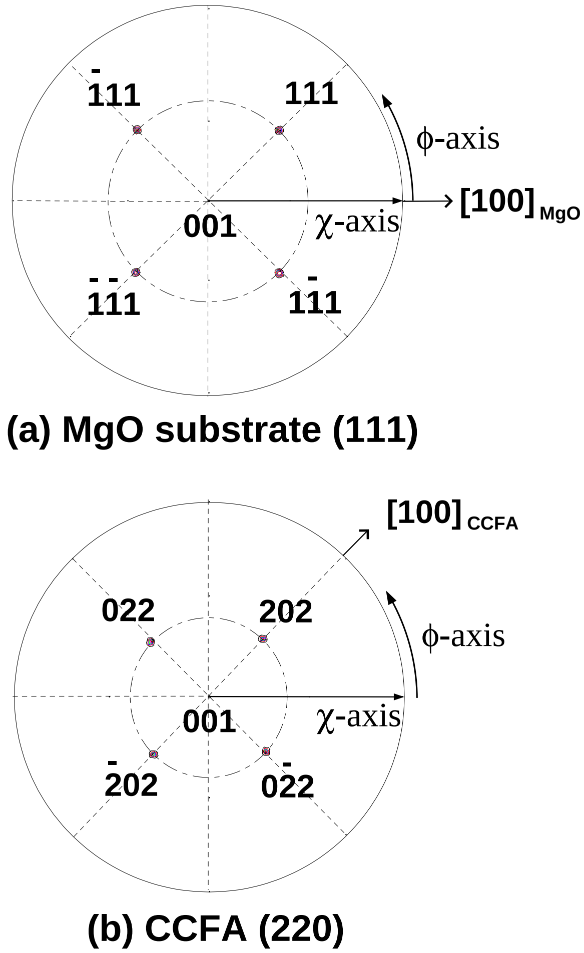

Fig. 3. X-ray pole figure measurement of (a) MgO (111) and (b) CCFA (220). Dot-dashed lines along ϕ axis indicate the tilt angle $\chi = 54.7^\circ$ for MgO(111) and $\chi = 45.0^\circ$ for CCFA (220). The [100] direction of the CCFA films is rotated by 45° from the MgO [100] direction.

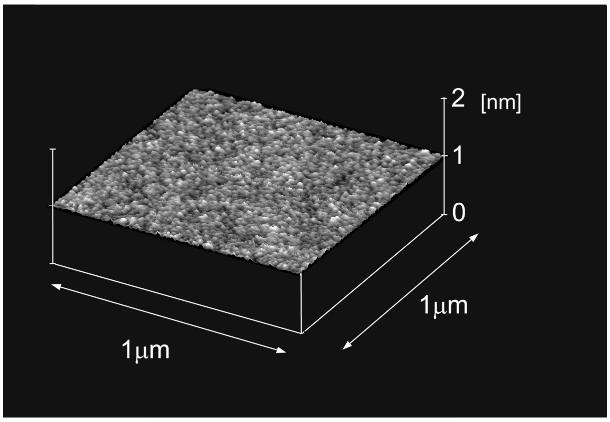

Fig. 4. Typical AFM image of the surface topography for a 100-nm-thick CCFA thin film annealed at 600°C.

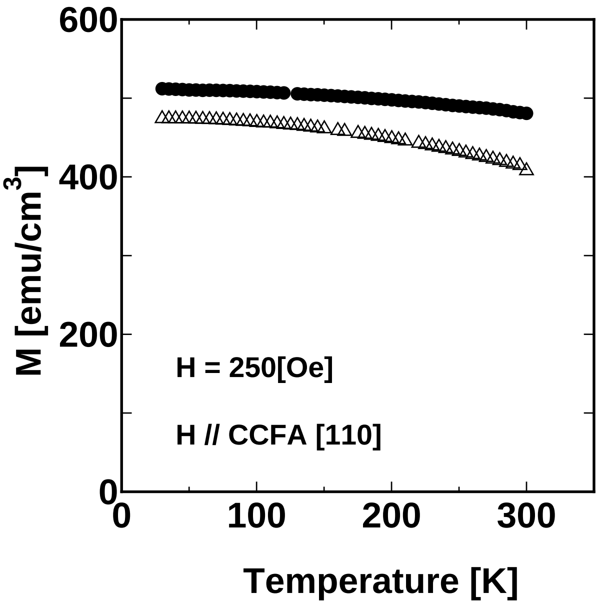

Fig. 5. Temperature dependence of magnetization for as-deposited film (△) and 500°C annealed film (●). Both sets of data were measured under a 250-Oe magnetic field.

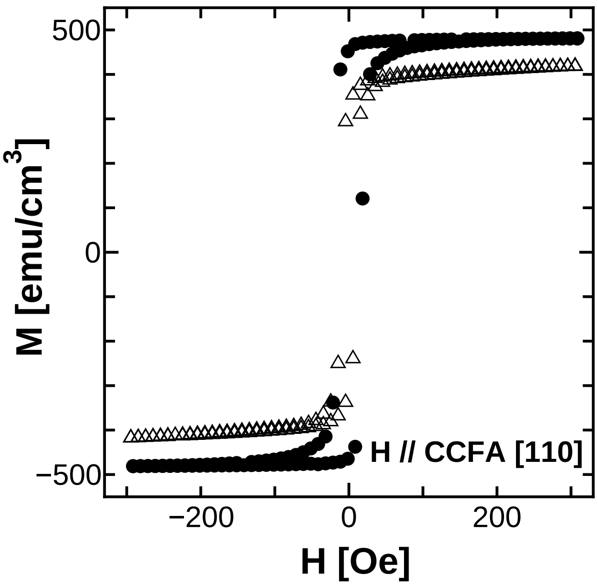

Fig. 6. Magnetic hysteresis curves for as-deposited film (△) and 500˚C-annealed film (•) at 300 K.