Preparation of YCo5 and GdCo5 Ordered Alloy Epitaxial Thin Films on Cu(111) Underlayer

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Y17Co83 and Gd17Co83 (at. %) alloy thin films are prepared on Cu(111) underlayers epitaxially grown on MgO(111) substrates at a substrate temperature of 500 °C by molecular beam epitaxy. The growth behavior and the film structure are investigated by in-situ reflection high-energy electron diffraction and X-ray diffraction. YCo5 and GdCo5 ordered alloy crystals epitaxially grow on the Cu underlayers. The epitaxial films consist of two (0001) variants whose orientations are rotated around the film normal by 30° each other. The epitaxial orientation relationships are (YCo5 or GdCo5)(0001)[1112] || Cu(111)[112] (type A) and (YCo5 or GdCo5)(0001)[1120] || Cu(111)[112] (type B). The volume ratios of two variants, Vtype A:VtypeB, in YCo5 and GdCo5 films are estimated to be 65:35 and 72:28, respectively. The long-range order degrees of YCo5 and GdCo5 films are respectively determined to be 0.63 and 0.65. These ordered alloy films show perpendicular magnetic anisotropies reflecting the magnetocrystalline anisotropies of YCo5 and GdCo5 crystals.

Key words: YCo5, GdCo5, ordered alloy, epitaxial thin film, perpendicular magnetic anisotropy

1. Introduction

Magnetic thin films with the easy magnetization axis perpendicular to the substrate surface and with the uniaxial magnetocrystalline anisotropy energy (Ku) greater than 10⁷ erg/cm³ have been investigated for applications like future recording media with the areal density exceeding 1 Tb/in². A bulk SmCo5 ordered alloy thin film formation was kept constant at 500 °C. Single-crystal substrates were prepared on polished MgO(111) substrates at a substrate temperature of 500 °C by molecular beam epitaxy. The growth behavior and the film structure are investigated by in-situ RHEED. The crystallographic properties during formations of SmT5 alloy thin films can be investigated by in-situ RHEED.

Ferromagnetic ordered alloys consisting of Co and R other than Sm with RT5 structure such as YCo5 and GdCo5 show Ku values greater than 10⁷ erg/cm³. However, there are few reports on the formations of (0001)-oriented RCo5 epitaxial films. In the present study, Y17Co83 and Gd17Co83 (at. %) materials are deposited on Cu(111) underlayers. The growth behavior and the film structure are investigated.

2. Experimental Procedure

Thin films were deposited on polished MgO(111) single-crystal substrates using an MBE system with the base pressure lower than 7 × 10⁻⁸ Pa. Pure Y (99.9%) and Gd (99.9%) metals were evaporated by electron beam heating, while pure Co (99.9%) and Cu (99.999%) materials were evaporated by using Knudsen cells. The film layer structures were Y17Co83(20 nm) /Cu(20 nm)/MgO(111) and Gd17Co83(20 nm)/Cu(20 nm) /MgO(111). MgO substrates were heated at 500 °C for 1 hour before film formation to obtain clean surfaces. 20-nm-thick Cu underlayers were deposited on the substrates. The epitaxial orientation relationships between Cu underlayer and MgO substrate were Cu(111)[112] || MgO(111)[112] and Cu(111)[112] || MgO(111)[112]. Y17Co83 and Gd17Co83 films of 20 nm thickness were formed by codeposition of Y and Co or Gd and Cu materials. The film composition was confirmed by energy dispersive X-ray spectroscopy to be within 17 ± 2 at. % R (R = Y or Gd), which is nearly the RCo5 stoichiometry. The substrate temperature during film formation was kept constant at 500 °C.
Fig. 2 [(a), (b)] RHEED patterns observed during formations of (a) Y17Co83 and (b) Gd17Co83 films on Cu(111) underlayers at 500 °C. The film thicknesses are [(a-1), (b-1)] 2, [(a-2), (b-2)] 5, [(a-3), (b-3)] 10, and [(a-4), (b-4)] 20 nm. The incident electron beam is parallel to MgO[11\_2] (|| Cu[11\_2], [1\_1\_2]). The intensity profiles of (c) and (d) are measured along the white dotted lines in (a-4) and (b-4), respectively.

Fig. 3 [(a-1)–(d-1), (a-2)–(d-2)] Schematic diagrams of RHEED patterns simulated for hexagonal (a) R2T17, (b) RT5, (c) R2T7, and (d) RT3 ordered alloy crystals of (0001) orientation by using the lattice constants of bulk R2T17 (a/2 = 0.42 nm, c/2 = 0.40 nm), RT5 (a = 0.50 nm, c = 0.40 nm), R2T7 (a = 0.50 nm, c/9 = 0.40 nm), and RT3 (a = 0.50 nm, c/6 = 0.40 nm) crystals. The incident electron beam is parallel to (a-1)–(d-1) [1\_1\_0] or (a-2)–(d-2) [1\_1\_2]. Schematic diagrams of (a-3)–(d-3) are drawn by overlapping (a-1)–(d-1) and (a-2)–(d-2), respectively.
The surface structure during film deposition was observed by RHEED. The resulting film structure was investigated by $2\theta$-$\phi$ scan out-of-plane, $2\theta/2\phi$ scan in-plane, and $\beta$-scan pole-figure X-ray diffractions (XRDs) with Cu-Kα radiation ($\lambda = 0.15418$ nm). The magnetization curves were measured by superconducting quantum interference device (SQUID) magnetometry.

3. Results and Discussion

Figures 2(a) and (b) show the RHEED patterns of Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ films deposited on Cu(111) underlayers observed by making the incident electron beam parallel to MgO[112] || Cu[112], [1T2]. Figure 3 shows the schematic diagrams of RHEED patterns simulated for hexagonal R$_{T5}$, R$_{T5}$, R$_{T5}$, and RT$_5$ ordered crystals of (0001) orientation. A clear RHEED pattern corresponding to the diffraction pattern simulated for RT$_5$(0001) surface [Fig. 3(b-3)] starts to be observed from the beginning of deposition and it remains unchanged until the end of film formation for both films. The Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ epitaxial films with RT$_5$ ordered structure are obtained. The observed RHEED patterns are analyzed to be an overlap of two reflections, as shown by the symbols, A and B, in the RHEED intensity profiles of Figs. 2(c) and (d). The crystallographic orientation relationships are thus determined as follows,

\[(\text{YCo}_5, \text{GdCo}_5)(0001)[11\bar{2}] || \text{Cu}(111)[1\bar{1}2], [1\bar{1}2] \quad \text{(type A)}\]
\[(\text{YCo}_5, \text{GdCo}_5)(0001)[1\bar{1}20] || \text{Cu}(111)[1\bar{1}2], [1\bar{1}2] \quad \text{|| } \text{MgO}(111)[1\bar{1}2]. \quad \text{(type B)}\]

The epitaxial films consist of two types of (0001) variant whose orientations are rotated around the film normal by 30° each other, which is similar to the growth of SmCo$_5$ film on Cu(111) underlayer.$^8,9$

The lattice misfit values of YCo$_5$ and GdCo$_5$ crystals with respect to Cu underlayer are respectively −3.4% and −2.9% in the A-type orientation relationship, whereas those are +11.5% and +12.2% in the B-type relationship. Here, the mismatches are calculated by using the lattice constants of bulk YCo$_5$ (a$_{\text{YCo5}} = 0.4937$ nm),$^{10}$ GdCo$_5$ (a$_{\text{GdCo5}} = 0.4963$ nm),$^{11}$ and Cu (a$_{\text{Cu}} = 0.3615$ nm)$^{12}$ crystals. Although there are fairly large mismatches in the cases of B-type YCo$_5$ and GdCo$_5$ variants, epitaxial growth is taking place. The intensity of RHEED from A-type variant is stronger than that from B-type variant for both materials [Figs. 2(c), (d)]. The nucleation of A-type variant with smaller lattice misfits seems to be favored.

In order to investigate the volume ratio of two types of variant, $\beta$-scan pole-figure XRD was carried out. Figure 4 shows the $\beta$-scan XRD patterns of Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ films measured by fixing the tilt and diffractions of $(\alpha, 2\theta B)$ at (45°, 30.5°), where YCo$_{11\bar{1}0}$ and GdCo$_{11\bar{1}0}$ reflections are expected to be detectable. Twelve (11\bar{1}0) reflections, which originate from the two types of variant, are observed with 30° separation for both films. The volume ratios of A-type to B-type variant in Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ films are estimated from the integrated intensities of (11\bar{1}0) reflections to be 65:35 and 72:28, respectively. It is revealed that the volume ratio of A-type variant is larger than that of B-type variant.

Figures 5(a-1) and (b-1) show the out-of-plane XRD patterns of Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ films, respectively. RT$_5$(0001) superlattice and RT$_5$(0002) fundamental reflections are clearly observed for both films. The out-of-plane XRD confirms the formations of YCo$_5$ and GdCo$_5$ ordered phases. Long-range order degree, S, is estimated by comparing the intensities of superlattice and fundamental reflections. The intensity (I) is proportional to structure factor and the complex absorption factor (A).$^{17}$ F(0001) and F(0002) are respectively calculated to be 0.63 and 0.65.

\[I_{RT5(0001)} / I_{RT5(0002)} = (FF LA)_{RT5(0001)} / (FF LA)_{RT5(0002)} \times (LA)_{RT5(0001)} / (LA)_{RT5(0002)}. \quad (1)\]

By solving this equation, S is given as

\[S = [I_{RT5(0001)} / I_{RT5(0002)}]^{1/2} \times [I_{RT5(0002)} / I_{RT5(0001)}]^{1/2} \times [L_{RT5(0002)} / L_{RT5(0001)}]^{1/2} \times [A_{RT5(0002)} / A_{RT5(0001)}]^{1/2}. \quad (2)\]

The S values of Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ films are respectively calculated to be 0.63 and 0.65.

Figures 5(a-2) and (b-2) show the in-plane XRD patterns of Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ films.
patterns measured by making the scattering vector parallel to MgO[110]. \( RT_5(1120) \) and \( RT_5(2240) \) reflections from A-type variant and \( RT_5(2200) \) and \( RT_5(3300) \) reflections from B-type variant are recognized for both films. The in-plane XRD confirms the epitaxial orientation relationship determined by RHEED.

Figure 6 shows the lattice constants, \( a \) and \( c \), of \( Y_{17}Co_{83} \) and \( Gd_{17}Co_{83} \) films, which are respectively estimated from the peak position angles of \( RT_5(2240) \) and \( RT_5(0000) \) reflections. Here, the lattice constants of bulk YCo, GdCo, \( Y_{0.6}Cu_{5.4} \), and GdCu5 crystals are cited from Refs. 15, 19, and 20. The \( a \) and \( c \) values of \( Y_{17}Co_{83} \) and \( Gd_{17}Co_{83} \) films are between those of bulk YCo5 and \( Y_{0.6}Cu_{5.4} \) crystals and between those of bulk GdCo5 and GdCu5 crystals, respectively. It is reported that Cu atoms of underlayer diffuse into Sm-Co film and partially substitute the Co site in SmCo5 structure forming an alloy compound of Sm(Co,Cu)5.45 The dissolution of Cu atom into Sm-Co alloy is known to stabilize \( RT_5 \) ordered structure.21–23 In the present case, Cu atoms are considered to have diffused from the underlayers into the \( Y_{17}Co_{83} \) and \( Gd_{17}Co_{83} \) films forming alloy compounds of \( Y(Co,Cu)_5 \) and \( Gd(Co,Cu)_5 \). It is necessary to confirm the element distribution by using a chemical analysis method.

Figure 7 shows the magnetization curves of \( Y_{17}Co_{83} \) and \( Gd_{17}Co_{83} \) films measured by applying the magnetic field along the perpendicular direction. These films are easily magnetized, which seems to be reflecting the easy magnetization axis of YCo5 and GdCo5 ordered alloy crystals.

4. Conclusion

\( Y_{17}Co_{83} \) and \( Gd_{17}Co_{83} \) thin films are deposited on Cu(111) underlayers at 500 °C. The film growth behavior and the detailed film structure are investigated by RHEED and XRD. YCo5 and GdCo5 ordered alloy epitaxial films of (0001) orientation are obtained. The films consist of two types of (0001) variant.
whose orientations are rotated around the film normal by 30° each other. The $S$ values of YCo$_5$ and GdCo$_5$ films are estimated to be 0.63 and 0.65, respectively. Cu atoms are considered to have diffused from the underlayers into the YCo$_5$ and GdCo$_5$ films and substitute the Co sites in YCo$_5$ and GdCo$_5$ structures forming alloy compounds of Y(Co,Cu)$_5$ and Gd(Co,Cu)$_5$. These ordered alloy films show perpendicular magnetic anisotropies reflecting the magnetocrystalline anisotropies of YCo$_5$ and GdCo$_5$ crystals.

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