Preparation of YCo$_5$ and GdCo$_5$ Ordered Alloy Epitaxial Thin Films on Cu(111) Underlayer

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Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ (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. YCo$_5$ and GdCo$_5$ 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 (YCo$_5$ or GdCo$_5$)(0001)[1100] || Cu(111)[112] (type A) and (YCo$_5$ or GdCo$_5$)(0001)[1120] || Cu(111)[112] (type B). The volume ratios of two variants, $V_{\text{type A}}:V_{\text{type B}}$, in YCo$_5$ and GdCo$_5$ films are estimated to be 65:35 and 72:28, respectively. The long-range order degrees of YCo$_5$ and GdCo$_5$ films are respectively determined to be 0.63 and 0.65. These ordered alloy films show perpendicular magnetic anisotropies reflecting the magnetocrystalline anisotropies of YCo$_5$ and GdCo$_5$ crystals.

**Key words:** YCo$_5$, GdCo$_5$, 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 ($K_u$) greater than $10^7$ erg/cm$^3$ have been investigated for applications like future recording media with the areal density exceeding 1 Tb/in$^2$. A bulk SmCo$_5$ ordered alloy material with RT$_5$-type (R: rare earth metal, T: transition metal) structure (Fig. 1) shows $K_u$ of $1.1 \times 10^8$ erg/cm$^3$ along the c-axis.$^{11}$ (0001)-oriented SmCo$_5$ polycrystalline$^{2-7}$ and epitaxial$^{8-10}$ films have been prepared on Cu,$^{2,5,7,8,9}$ Ru,$^{6,7,10}$ and Ru/Cr$_{15}$ underlayers.

The Sm and Co sites in SmCo$_5$ structure can be replaced with other R and T elements, respectively. In our previous studies, SmFe$_5$$^{11-13}$ and SmNi$_5$$^{11,14}$ ordered alloy epitaxial films were prepared on Cu(111) underlayers by using a molecular beam epitaxy (MBE) system equipped with a reflection high-energy electron diffraction (RHEED) facility. The crystallographic properties during formations of SmT$_5$ alloy films can be investigated by in-situ RHEED.

Ferromagnetic ordered alloys consisting of Co and R other than Sm with RT$_5$ structure such as YCo$_5$ and GdCo$_5$ also show $K_u$ values greater than $10^7$ erg/cm$^3$. However, there are few reports on the formations of (0001)-oriented RCo$_5$ epitaxial films. In the present study, Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ (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 $7 \times 10^{-9}$ Pa. Pure Y (99.9%) and Gd (99.9%) metals were evaporated by electron beam heating, while pure Co (99.9%) and Cu (99.9999%) materials were evaporated by using Knudsen cells.

The film layer structures were Y$_{17}$Co$_{83}$(20 nm)/Cu(20 nm)/MgO(111) and Gd$_{17}$Co$_{83}$(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]. Y$_{17}$Co$_{83}$ and Gd$_{17}$Co$_{83}$ films of 20 nm thickness were formed by co-evaporation of Y and Co or Gd and Co materials. The film composition was confirmed by energy dispersive X-ray spectroscopy to be within $17 \pm 2$ at. % R ($R = Y$ or Gd), which is nearly the RCo$_5$ stoichiometry. The substrate temperature during film formation was kept constant at 500 °C.
Fig. 2 [(a), (b)] RHEED patterns observed during formations of (a) Y$_{17}$Co$_{83}$ and (b) Gd$_{17}$Co$_{83}$ 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[1120] (|| Cu[1120], [1121]). 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) R$_2$T$_7$, (b) RT$_5$, (c) R$_2$T$_3$, and (d) RT$_3$ ordered alloy crystals of (0001) orientation by using the lattice constants of bulk R$_2$T$_7$ (a/2 = 0.42 nm, c/2 = 0.40 nm), RT$_5$ (a = 0.50 nm, c = 0.40 nm), R$_2$T$_3$ (a = 0.50 nm, c/6 = 0.40 nm), and RT$_3$ (a = 0.50 nm, c/6 = 0.40 nm) crystals. The incident electron beam is parallel to (a-1)–(d-1) [1100] or (a-2)–(d-2) [1120]. 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 \(2\theta\omega\)-scan out-of-plane, \(2\theta\varphi\)-scan in-plane, and \(\beta\)-scan pole-figure X-ray diffractions (XRDs) with Cu-K\(\alpha\) 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 \(\text{Y}_{17}\text{Co}_{83}\) and \(\text{Gd}_{17}\text{Co}_{83}\) films deposited on Cu(111) underlayers observed by making the incident electron beam parallel to MgO[11\(\bar{2}\)] (|| Cu[11\(\bar{2}\)], [1\(\bar{2}\)2]). Figure 3 shows the schematic diagrams of RHEED patterns simulated for hexagonal \(\text{R}_{2}\text{Ti}_{7}, \text{R}_{3}\text{Ti}_{7}, \text{R}_{2}\text{Ti}_{5}\), and \(\text{R}_{5}\text{Ti}_{3}\) ordered crystals of (0001) orientation. A clear RHEED pattern corresponding to the diffraction pattern simulated for \(\text{RT}_{5}(0001)\) 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. \(\text{Y}_{17}\text{Co}_{83}\) and \(\text{Gd}_{17}\text{Co}_{83}\) epitaxial films with (0001) orientation relationship. Here, the mismatches are calculated by using the lattice constants of bulk YCo\(_5\) (\(a_{\text{YCo}_5} = 0.4937\) nm),\(^{15}\) GdCo\(_5\) (\(a_{\text{GdCo}_5} = 0.4963\) nm),\(^{15}\) and Cu (\(a_{\text{Cu}} = 0.3615\) nm)\(^{15}\) crystals. Although there are fairly large lattice misfits in the cases of B-type YCo\(_5\) and GdCo\(_5\) variants, epitaxial growth is taking place. The intensity is shown in linear scale.

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.\(^{8,9}\)

\[
\frac{\alpha}{\beta} = \frac{S}{2}\left[\frac{f_R - f_T}{f_R + 5f_T}\right]^2
\]

where \(f\) is the atomic scattering factor. Therefore, \(I_{0001}/I_{0002}\) is expressed as

\[
I_{0001}/I_{0002} = \left(\frac{FF^*LA}{RT_{5}(0001)}\right)\rho \times \left(\frac{LA}{RT_{5}(0002)}\right)\rho
\]

By solving this equation, \(S\) is given as

\[
S = \rho \left[\frac{LA}{RT_{5}(0001)}\right]^{1/2} \times \frac{I_{0001}/I_{0002}}{LA/RT_{5}(0002)}
\]

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

Figures 5(a-1) and (b-1) show the out-of-plane XRD patterns of \(\text{Y}_{17}\text{Co}_{83}\) and \(\text{Gd}_{17}\text{Co}_{83}\) films, respectively. \(\text{RT}_{5}(0001)\) superlattice and \(\text{RT}_{5}(0002)\) 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 is proportional to structure factor and the complex conjugate \((FF^*)\), Lorentz-polarization factor \((L)\), and absorption factor \((\rho)\).\(^{17}\) \(F_{0001}\) and \(F_{0002}\) are respectively \(S(\beta - f)\) and \((\beta + 5\beta_f)^2\), where \(f\) is the atomic scattering factor. Therefore, \(I_{0001}/I_{0002}\) is expressed as

\[
I_{0001}/I_{0002} = \left(\frac{FF^*LA}{RT_{5}(0001)}\right)\rho \times \left(\frac{LA}{RT_{5}(0002)}\right)\rho
\]

and fundamental reflections. The intensity is shown in linear scale.
patterns measured by making the scattering vector parallel to \( \text{MgO(110)} \). \( RT_5(11 \overline{2} 0) \) and \( RT_5(22 \overline{4} 0) \) reflections from A-type variant and \( RT_5(2 2 0 0) \) and \( RT_5(3 \overline{3} 0 0) \) 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 \( Y_{17}\text{Co}_{83} \) and \( \text{Gd}_{17}\text{Co}_{83} \) 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\(_{0.8}\)Cu\(_{5.4}\), and GdCu\(_5\) crystals are cited from Refs. 15, 19, and 20. The \( a \) and \( c \) values of \( Y_{17}\text{Co}_{83} \) and \( \text{Gd}_{17}\text{Co}_{83} \) films are between those of bulk YCo\(_5\) and Y\(_{0.8}\)Cu\(_{5.4}\) crystals and between those of bulk GdCo and GdCu\(_5\) crystals, respectively. It is reported that Cu atoms of underlayer diffuse into Sm-Co film and partially substitute the Co site in SmCo\(_5\) structure forming an alloy compound of Sm(0.4Cu)\(_{5}\).\(^{4,50}\) 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 \( Y_{17}\text{Co}_{83} \) and \( \text{Gd}_{17}\text{Co}_{83} \) films forming alloy compounds of Y(0.4Cu)\(_5\) and Gd(0.4Cu)\(_5\). It is necessary to confirm the element distribution by using a chemical analysis method.

Figure 7 shows the magnetization curves of \( Y_{17}\text{Co}_{83} \) and \( \text{Gd}_{17}\text{Co}_{83} \) 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 YCo\(_5\) and GdCo\(_5\) ordered alloy crystals.

4. Conclusion

\( Y_{17}\text{Co}_{83} \) and \( \text{Gd}_{17}\text{Co}_{83} \) 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. YCo\(_5\) and GdCo\(_5\) 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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References

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