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Thermal stability of $L1_1$ ordered phase in CoPt-alloy thin films formed on MgO(111) single-crystal substrates

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Abstract. Metastable $L1_1$ ordered CoPt(111) epitaxial thin films with the order degrees around 0.3 are formed on MgO(111) single-crystal substrates at 300 °C by using an ultra-high vacuum radio-frequency magnetron sputtering system. The effects of annealing after film formation on the structure and the magnetic properties are investigated. As the annealing temperature increases, the order degree gradually decreases. At 600 °C, the ordered phase disappears and the film changes to disordered structure. CoPt(111) epitaxial films with disordered structure are also prepared at room temperature and 600 °C and then these films are annealed at 300 °C. However, ordered phase formation is not recognized in the films. The metastable $L1_1$ ordered phase is preferentially formed when the film is deposited at a temperature of 300 °C. Annealing a film with disordered structure at 300 °C does not promote $L1_1$ ordering. The CoPt films involving $L1_1$ ordered structure show perpendicular magnetic anisotropies, whereas the disordered films have in-plane anisotropies. The magnetic properties are influenced by the order degree.

1 Introduction

Perpendicularly magnetized thin films with high uniaxial magnetocrystalline anisotropy energies (K_u) have been investigated for applications like high-density magnetic recording media, magnetic random access memory devices, etc. Recently, metastable $L1_1$ ordered CoPt-alloy films have attracted much attention for such applications [1]–[6], since an $L1_1$-CoPt film with order degree of 0.33 shows K_u of 1.7×10^7 erg/cm^3 along the direction normal to the close-packed plane and the K_u increases with increasing the order degree [2]. The $L1_1$ ordered phase is preferentially formed in CoPt films deposited around 300 °C [1]–[5]. The thermal stability of $L1_1$ ordered phase after film formation is also an important property for practical device applications such as heat-assisted magnetic recording media. In the present study, $L1_1$ ordered CoPt-alloy epitaxial films are formed on MgO(111) single-crystal substrates at a substrate temperature of 300 °C. Disordered CoPt epitaxial films are also prepared at substrate temperatures of room temperature (RT) and 600 °C. The effects of annealing on the structure and the magnetic properties are investigated.

2 Experimental procedure

CoPt-alloy films of 40 nm thickness were prepared on MgO(111) substrates by using a radio-frequency (RF) magnetron sputtering system equipped with a reflection high-energy electron diffraction (RHEED) facility. The base pressures were lower than 4×10^{-7} Pa. Before film formation, substrates were heated at 600 °C for 1 h in the chamber to obtain clean surfaces. A $Co_{50}Pt_{50}$ (at. %) target of 3 in. diameter was employed. The distance

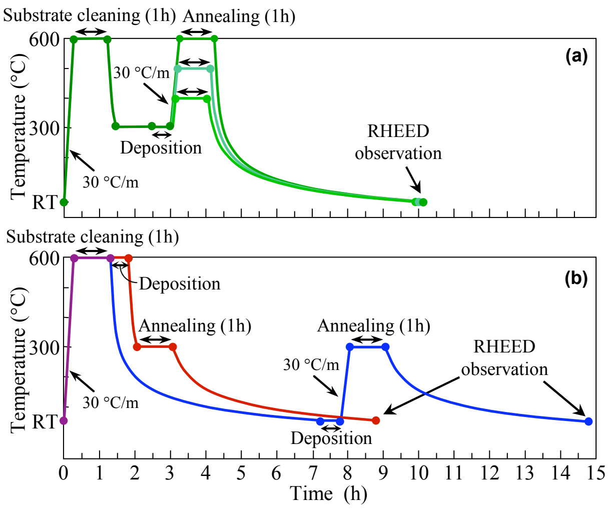

Fig. 1. Time-temperature programs for preparation of (a) CoPt films deposited at 300 °C followed by annealing at temperatures ranging between 400 and 600 °C and (b) CoPt films deposited at RT and 600 °C followed by annealing at 300 °C.

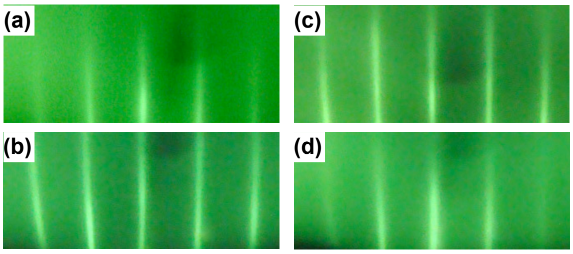

Fig. 2. RHEED patterns observed for (a) a CoPt film deposited at 300 °C and (b)–(d) CoPt films annealed at (b) 400, (c) 500, and (d) 600 °C after deposition at 300 °C. The incident electron beam is parallel to MgO[$1\bar{1}0$] direction.

between target and substrate was 150 mm. The Ar gas pressure and the RF power were respectively fixed at 0.67 Pa and 45 W, where the deposition rate was 0.02 nm/s. CoPt-alloy films were deposited on MgO(111) substrates at 300 °C and then the films were annealed at temperatures ranging from 400 to 600 °C for 1 h, as shown in figure 1(a). CoPt-alloy films were also prepared on MgO substrates at RT and 600 °C and the films were annealed at 300 °C for 1 h, as shown in figure 1(b). The film compositions were confirmed by energy dispersive X-ray spectroscopy and the errors were less than 4 at. % from the target composition.

The surface structure was studied by RHEED. The film structure was investigated by $2\theta/\omega$-scan (out-of-plane) and pole-figure X-ray diffraction (XRD) with Cu-Kα radiation (λ = 0.15418 nm). The magnetization curves were measured by using a vibrating sample magnetometer.

The notations of crystallographic plane and direction are different between disordered ($A1$) and ordered ($L1_1$) structures. In the present study, $A1$-based lattice notation is employed for the $L1_1$ structure for simple comparison with the $A1$ structure.

3 Results and discussion

3.1 CoPt films annealed at different temperatures after deposition at 300 °C

Figure 2(a) shows the RHEED pattern observed for a CoPt film deposited on MgO(111) substrate at 300 °C. A clear diffraction pattern consisting of only streaks is observed. The pattern does not correspond to $L1_0(111)$ texture but $A1(111)$, $L1_1(111)$, $A3(0001)$, or $B_h(0001)$ texture, as shown in the RHEED spot maps of figure 3. Here, $A1$ and $L1_1$ are respectively fcc-based disordered and ordered structures, whereas $A3$ and B_h are respectively hcp-based disordered and ordered structures. A CoPt epitaxial film with the close-packed plane parallel to the substrate surface is obtained. When a streak pattern is observed, it is not easy to determine the diffraction pattern to be one of the textures, $A1(111)$, $L1_1(111)$, $A3(0001)$, and $B_h(0001)$, since the diffraction patterns from these textures are very similar. The crystal structure is thus determined from the viewpoints of atomic stacking sequence of close-packed plane and order degree. The stacking sequence is investigated by pole-figure XRD, while the order degree is measured by out-of-plane

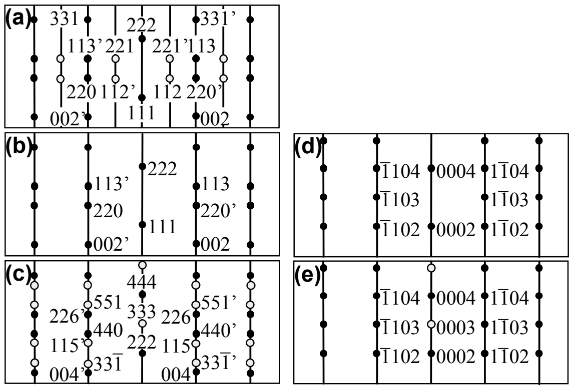

Fig. 3. RHEED spot maps corresponding to (a) $L1_0(111)$, (b) $A1(111)$, (c) $L1_1(111)$, (d) $A3(0001)$, and (e) $B_h(0001)$ surfaces. The incident electron beam is parallel to (a) [$1\bar{1}0$], [$\bar{1}10$], [$\bar{1}01$], [$10\bar{1}$], [$01\bar{1}$], and [$0\bar{1}1$], (b, c) [$1\bar{1}0$] and [$\bar{1}10$], or (d, e) [$11\bar{2}0$] direction. The filled and the open circles correspond to fundamental and superlattice reflection spots, respectively.

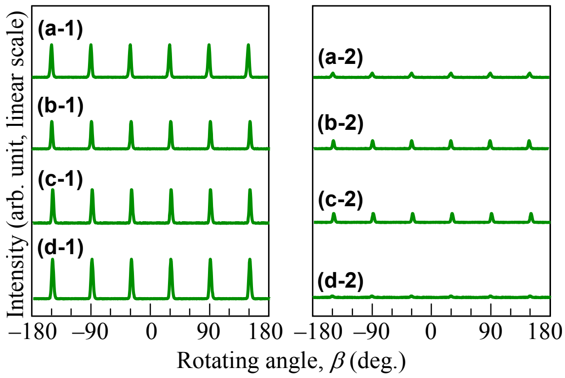

Fig. 4. Pole-figure XRD spectra of (a) a CoPt film deposited at 300 °C and (b)–(d) CoPt films annealed at (b) 400, (c) 500, and (d) 600 °C after deposition at 300 °C. The spectra are measured by fixing the tilt and the diffraction angles, (α, $2\theta B$), at (a-1, b-1, c-1, d-1) (20°, 42°) or (a-2, b-2, c-2, d-2) (28°, 45°). The intensity is shown in a linear scale.

XRD. Figure 4(a) shows the pole-figure XRD spectra measured by fixing the tilt and the diffraction angles, (α, $2\theta B$), at (20°, 42°) and (28°, 45°), where $\{222\}_{A1 \text{ or } L11}$ and $\{1\bar{1}01\}_{A3 \text{ or } Bh}$ reflections are expected to be detectable, respectively. The details of measurement conditions are explained in our previous work [7]. Strong six reflections which originate from two $(111)_{A1 \text{ or } L11}$ variants with a three-fold symmetry with respect to the perpendicular direction are recognized with 60° separation in the spectrum of figure 4(a-1), whereas almost no reflections from $A3$ or B_h crystal are observed in the spectrum of figure 4(b-1). The result shows that the film consists of two variants whose atomic stacking sequences are ABCABC... and ACBACB... (i.e. $A1$ or $L1_1$), involving very small amounts of stacking fault. Figure 5(a) shows the out-of-plane spectrum. A superlattice reflection from CoPt film is recognized around the diffraction angle, 2θ, of 21° in addition to fundamental reflections existing around 2θ of 42° and 92°, indicating that an ordered phase is formed in the film. The crystal structure and the orientation relationship of CoPt film with respect to MgO(111) substrate are thus determined from the

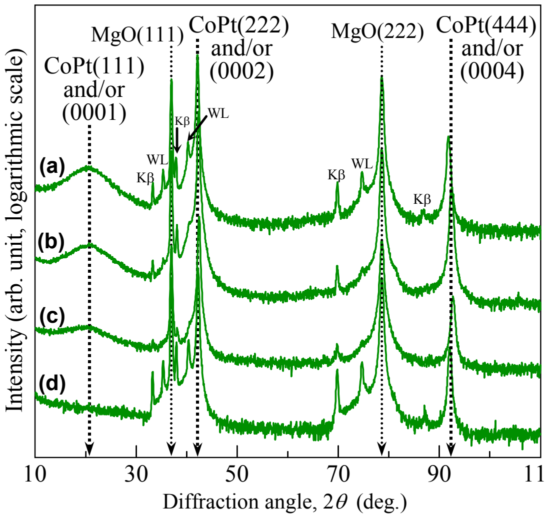

Fig. 5. Out-of-plane XRD spectra of (a) a CoPt film deposited at 300 °C and (b)–(d) CoPt films annealed at (b) 400, (c) 500, and (d) 600 °C after deposition at 300 °C. The intensity is shown in a logarithmic scale.

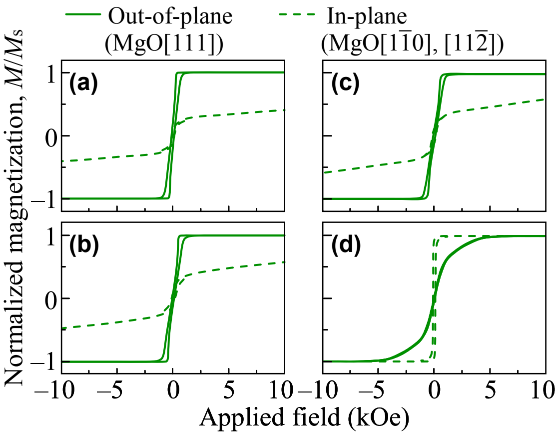

Fig. 6. Magnetization curves of (a) a CoPt film deposited at 300 °C and (b)–(d) CoPt films annealed at (b) 400, (c) 500, and (d) 600 °C after deposition at 300 °C. There are no difference between the hysteresis curves measured along MgO[1$\bar{1}$0] and MgO[11$\bar{2}$].

viewpoints of atomic stacking sequence and order degree as

$$L1_1\text{-CoPt}(111)[1\bar{1}0], (111)[\bar{1}10] \parallel \text{MgO}(111)[1\bar{1}0].$$

The long-range order degree (S) is calculated to be 0.30. The calculation method is shown in our previous paper [6].

Figures 2(b)–(d) show the RHEED patterns observed for CoPt films annealed at different temperatures after deposition at 300 °C. Clear diffraction patterns similar to the case of CoPt film deposited at 300 °C are observed for all the films. Figures 4(b)–(d) show the pole-figure XRD spectra. The annealed films also consist primarily of atomic stacking sequences of ABCABC... and ACBACB... Figures 5(b)–(d) show the out-of-plane spectra. As the annealing temperature increases, the intensity of superlattice reflection gradually decreases. When the annealing temperature is set at 600 °C, no superlattice reflections are observed. The $L1_1$ phase is

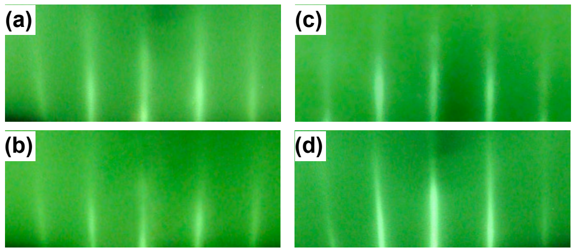

Fig. 7. RHEED patterns observed for (a, c) CoPt films deposited at (a) RT and (c) 600 °C and (b, d) CoPt films annealed at 300 °C after deposition at (b) RT and (d) 600 °C. The incident electron beam is parallel to MgO[1$\bar{1}$0] direction.

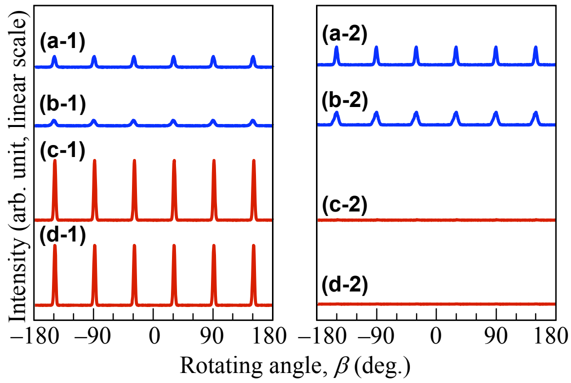

Fig. 8. Pole-figure XRD spectra of (a, c) CoPt alloy films deposited at (a) RT and (c) 600 °C and (b, d) CoPt films annealed at 300 °C after deposition at (b) RT and (d) 600 °C. The pole-figure XRD spectra are measured by fixing the tilt and the diffraction angles, (α, $2\theta B$), at (a-1, b-1, c-1, d-1) (20°, 42°) or (a-2, b-2, c-2, d-2) (28°, 45°). The intensity is shown in a linear scale.

apparently transforming into $A1$ phase in the crystallographic orientation relationship of

$$A1\text{-CoPt}(111)[1\bar{1}0], (111)[\bar{1}10] \parallel L1_1\text{-CoPt}(111)[1\bar{1}0], (111)[\bar{1}10].$$

The S values of CoPt films annealed at 400, 500, and 600 °C are 0.23, 0.17, and 0, respectively.

Figure 6 shows the magnetization curves of CoPt films before and after annealing. The films before annealing and after annealing at temperatures lower than 500 °C show perpendicular magnetic anisotropies, since these films include $L1_1$ phase. On the other hand, the film annealed at 600 °C shows an in-plane magnetic anisotropy. This is because the film consists of an $A1$ crystal transformed from $L1_1$ phase by high-temperature annealing at 600 °C. The magnetization property is influenced by the crystal structure.

3.2 CoPt films annealed at 300 °C after deposition at RT and 600 °C

Figures 7(a) and (b) show the RHEED patterns observed for a CoPt film deposited at RT and the film annealed at 300 °C after RT deposition. Clear RHEED patterns are observed for both films. Figures 8(a) and (b) show the pole-figure XRD spectra. These films consist of a mixture of atomic stacking sequences of ABCABC..., ACBACB..., and ABAB... Figures 9(a) and (b) show the

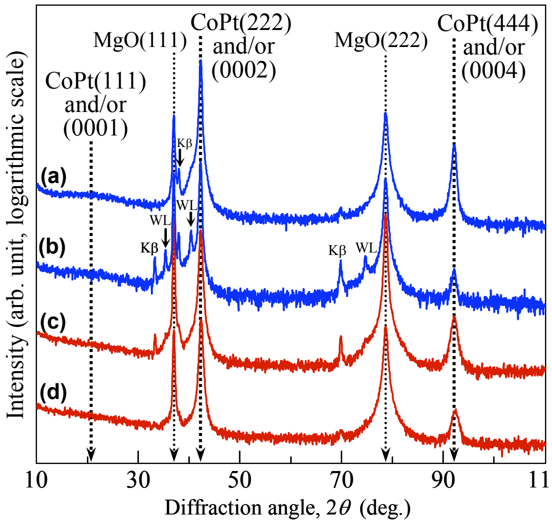

Fig. 9. Out-of-plane XRD spectra of (a, c) CoPt alloy films deposited at (a) RT and (c) 600 °C and (b, d) CoPt films annealed at 300 °C after deposition at (b) RT and (d) 600 °C. The intensity is shown in a logarithmic scale.

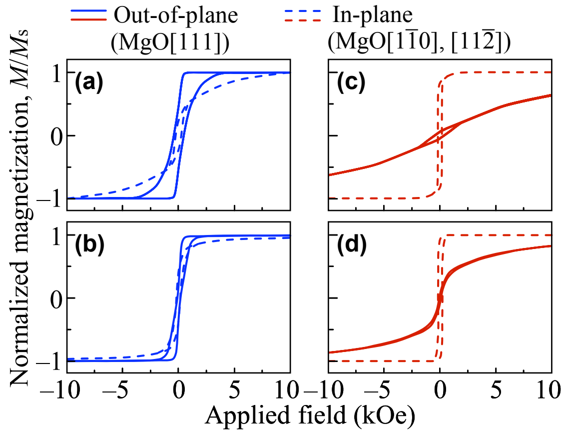

Fig. 10. Magnetization curves of (a, c) CoPt films deposited at (a) RT and (c) 600 °C and (b, d) CoPt films annealed at 300 °C after deposition at (b) RT and (d) 600 °C. There are no difference between the hysteresis curves measured along MgO[1$\bar{1}$0] and MgO[11$\bar{2}$].

out-of-plane XRD spectra. A very weak superlattice reflection is recognized for the CoPt film deposited at RT. The result shows that the order degree is very low. The S value is estimated to be lower than 0.1. On the contrary, no superlattice reflections are observed for the film annealed at 300 °C. Therefore, the both films, one is prepared by deposition at RT and the other is annealed at 300 °C after RT deposition, consist of a mixture of $A1$ and $A3$ disordered phases. The film deposited at RT includes a small volume of $L1_1$ and B_h ordered phases. The crystallographic orientation relationships of CoPt film with respect to MgO substrate are determined as

$$A1\text{-CoPt}(111)[1\bar{1}0],\ (111)[\bar{1}10] \parallel \text{MgO}(111)[1\bar{1}0],$$
$$L1_1\text{-CoPt}(111)[1\bar{1}0],\ (111)[\bar{1}10] \parallel \text{MgO}(111)[1\bar{1}0],$$
$$A3\text{-CoPt}(0001)[11\bar{2}0] \parallel \text{MgO}(111)[1\bar{1}0],$$
$$B_h\text{-CoPt}(0001)[11\bar{2}0] \parallel \text{MgO}(111)[1\bar{1}0].$$

Figures 10(a) and (b) show the magnetization curves. These films show perpendicular magnetic anisotropies. The reason is due to that the films involve $A3(0001)$ crystals whose easy magnetization axis is perpendicular to the (0001) plane.

Figures 7(c) and (d) show the RHEED patterns observed for a CoPt film deposited at 600 °C and the film annealed at 300 °C after 600 °C deposition. Clear diffraction patterns are recognized for both films. Figures 8(c), (d), 9(c), and (d) show the pole-figure and the out-of-plane XRD spectra. The data indicate that these films are with disordered $A1$ phase and do not include ordered phases. Figures 10(c) and (d) show the magnetization curves. These films show in-plane magnetic anisotropies.

The present study has shown that metastable $L1_1$ ordered phase is preferentially formed when films are deposited at a temperature of 300 °C. It is also made clear that annealing a film with disordered structure at 300 °C does not effectively enhance $L1_1$ ordering.

4 Conclusions

Metastable $L1_1$ ordered CoPt films are formed on MgO(111) substrates at 300 °C. The effect of annealing on the stability of $L1_1$ ordered phase is investigated. With increasing the annealing temperature, the order degree decreases. When the annealing temperature is set at 600 °C, the ordered phase disappears. Disordered CoPt films are also prepared at substrate temperatures of RT and 600 °C and then these films are annealed at 300 °C. However, no ordered phase is formed in the films after annealing at 300 °C. The metastable $L1_1$ ordered phase is preferentially formed when films are deposited at 300 °C.

Acknowledgments

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References

1. S. Iwata, S. Yamashita, S. Tsunashima, IEEE Trans. Magn. **33**, 3670 (1997)
2. H. Sato, T. Shimatsu, Y. Okazaki, H. Muraoka, H. Aoi, S. Okamoto, O. Kitakami, J. Appl. Phys. **103**, 07E114 (2008)
3. A. -C. Sun, F. -T. Yuan, J. -H. Hsu, H. Y. Lee, Scripta Mater. **61**, 713 (2009)
4. M. Ohtake, S. Ouchi, F. Kirino, M. Futamoto, IEEE Trans. Magn. **48** (2012) [Proc. Intermag 2012, EH-01, DOI: 10.1109/TMAG.2012.2198875] (to be published)
5. D. Suzuki, M. Ohtake, F. Kirino, M. Futamoto, IEEE Trans. Magn. **48** (2012) [Proc. Intermag 2012, BS-02, DOI: 10.1109/TMAG.2012.2201216] (to be published)
6. F. -T. Yuan, A. -C. Sun, J. -H. Hsu, Scripta Mater. **62**, 762 (2010)
7. M. Ohtake, O. Yabuhara, Y. Nukaga, M. Futamoto, J. Phys.: Conf. Ser. **303**, 012016 (2011)