Evolution of structure and magnetic properties of sputter-deposited CoPt thin films on MgO(1 1 1) substrates: Formation of the L₁ phase

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CoPt thin films with a thickness of 50 nm were deposited on MgO(111) substrates by magnetron-sputtering at temperatures ranging from room temperature to 750 °C. A unique phase evolution of A1 (disordered) → L₁ → A1 → L₁₀ was clearly identified by performing θ – 2θ scans at different ψ angles using a Huber goniometer. The L₁ CoPt phase with perpendicular magnetocrystalline anisotropy can be developed at 250 °C, thus making it a promising material for future ultra-high-density magnetic recording media. © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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The demand for ultra-high-density magnetic recording media explains why materials with high magnetocrystalline anisotropy (MCA) have received considerable attention. L₁₀ ordered alloys such as FePt and CoPt are regarded as promising alternatives to replace the currently used CoCrPt media in future magnetic recording applications with an ultrahigh density exceeding 1 Tbits in^{−2}, owing to their large MCA ($>4 \times 10^6$ J m^{−3}) [1], high Curie temperature (>450 °C) and higher chemical stability. However, the processing temperatures at which the L₁₀ phase forms – above 350 °C for FePt and above 520 °C for CoPt – are too high to enable these alloys to be used in the recording industry.

A previously discovered phase of CoPt L₁ offers an alternative, first reported upon by Iwata et al. It is a metastable ordered phase that is formed in epitaxially grown thin films deposited by MBE at temperatures ranging from 200 to 400 °C [2]. The crystal structure was determined to be a CuPt-type rhombohedral lattice, whose unit cell consists of alternating close-packed atomic layers of Co and Pt along the [1 1 1] direction. The angle α between the crystal axes of the rhombohedral cell and lattice parameter a were estimated to be 61.5° and 0.534 nm,

respectively. The ABC stacking structure of CuPt type exhibits a very large perpendicular MCA of approximately 2×10^6 J m^{−3} [2]. Huang et al. also used MBE to grow films with the L₁ phase on the (11–20), (1–102) and (1–100) surfaces of Al₂O₃ substrates at growth temperatures of around 300 °C [3]. Enhanced perpendicular magnetic anisotropy has also been described. Shimatsu et al. has demonstrated recently that the CoPt L₁ phase can also be formed by sputter deposition on various substrates of MgO(1 1 1) and glass with Pt and Ru underlayers [4]. A maximum MCA of about 3.7×10^6 J m^{−3} was measured at the equiatomic composition, whose value is around an order of magnitude larger than that of CoCrPt-based films that are currently used in the medium. Although L₁ CoPt is highly promising for perpendicular magnetic recording applications, many of its major characteristics have not been determined, such as its order parameter and structural variation with temperature. The L₁ phase is reportedly eliminated when the growth temperature reaches 500 °C [2]. X-ray diffraction patterns indicate that the L₁ phase may transform into two possible phases – A1 and L₁₀. Although Iwata et al. have claimed that L₁ phase changes into L₁₀ phase [2], their conclusion has not been well verified. Thermodynamically, the L₁₀ structure should be the equilibrium phase of CoPt at room temperature. The appearance of the L₁ phase at low temperatures makes the evolution

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of the structure more complex than the well-known transformation from A1 to L1₀ in CoPt and FePt. This study elucidates the entire evolution of the structure of sputter-deposited CoPt thin films on MgO(1 1 1) substrates. The corresponding variation in the magnetic properties is also described.

CoPt thin films were deposited on MgO(1 1 1) substrates using dc magnetron sputtering. The background pressure was lower than 2.5×10^{-7} Pa, and the working pressure was fixed at 1.3 Pa. The substrate temperature (T_s) was varied from room temperature (RT) to 750 °C to examine the complete evolution of the structure. The CoPt layer was grown by co-sputtering using Pt and Co targets with a high purity of 99.999at.%. The chemical composition of the CoPt layer was controlled by adjusting the sputtering powers of the Co and Pt targets and it was determined by energy dispersion spectroscopy (EDS) to be Co₄₈Pt₅₂. The thickness of the CoPt films was 50 nm. The phase was identified by X-ray diffractometry (XRD) using the 8-circle diffractometer at beamline 17B1 of the National Synchrotron Radiation Research Center (NSRRC). The beam energy was 8 keV with the wavelength $\lambda = 0.15$ nm. The beam spot size was around 0.25×0.8 mm, and energy resolution $\Delta E/E$ was in the order of 10^{-4} . The step interval was 0.025° and the collection time for each step was 1 s. The intensity of the diffraction patterns was normalized to the intensity of the incident beam after the measurements had been made. The peak positions were determined by pseudo-Voigt function fitting. Magnetic measurements were made on a vibrating sample magnetometer (VSM) at RT and superconducting quantum interference device (SQUID) at RT and 4 K with maximum applied fields of about 1.6 MA m^{-1} and 4.0 MA m^{-1} , respectively.

In this study, three structures, A1, L1₁, and L1₀, have been observed in the CoPt films that had been prepared at various temperatures. Conventional θ -2 θ X-ray diffraction reveals the formation of L1₁ phase by the presence of superlattice peaks of (1 1 1) and (3 3 3). However, it fails to distinguish between A1 and L1₀ phases because the two fundamental peaks of (1 1 1) and (2 2 2) of these two phases are very close to each other and are the only peaks present in the XRD patterns. In order to distinguish A1 and L1₀ phases, the superlattice diffractions such as (0 0 1) and (1 1 0) of the ordered phase must be examined. A (6 + 2) Huber goniometer was employed to obtain (0 0 1), (1 1 0), {2 0 0}, and {2 2 0} diffraction peaks in a (1 1 1)-textured samples with χ -rotation. Figure 1a shows the diffraction geometry and definitions of various angles as well as axes, where χ -axis is the intersection of the film and scattering planes. By adjusting the ψ angle, the angle between film normal direction and scattering plane, to the normal directions of (0 0 1)/{2 0 0} or (1 1 0)/{2 2 0}, the related fundamental and superlattice peaks can be detected. To detect (0 0 1)/{2 0 0} diffractions, the χ -axis should be rotated from $\psi = 0^\circ$ (normal to the film surface) to 54.7° , as shown in Figure 1b. To examine the (1 1 0)/{2 2 0} group, the rotation angle should be 34.9° . Additionally, the distinct symmetry between cubic and rhombohedral lattices as illustrated in Figure 1b and c enables us to identify A1, L1₀, and L1₁ phases.

Figure 1. (a) A schematic illustration to elucidate the diffraction geometry and definitions of various angles as well as axis; (b) and (c) are illustrations to elucidate different symmetries between A1 and L1₁ structures.

Figure 2 displays the XRD results for the CoPt films grown on MgO(1 1 1) substrates at various temperatures from RT to 750 °C. The CoPt film grown at RT yields three fundamental peaks associated with (1 1 1), (2 0 0), and (2 2 0), indicating the disordered A1 structure. The peak intensities are low due to poor crystallization, which was caused by the low temperature of deposition. The lattice parameter a is about 3.76 Å. As T_s was increased to 200 °C, the structure of the film remained disordered. The intensities of the three fundamental peaks and the 2θ angles were increased. A reduced lattice parameter was determined to be 3.74 Å, which may be associated with the relaxation of the internal strain or stress arising from the lattice mismatch between the MgO substrate and the CoPt film. A superlattice peak from the (1 1 1) plane of the L1₁ phase appeared at $2\theta = 20.43^\circ$ from the film with $T_s = 250$ °C, revealing the onset of L1₁ ordering. Notably, the abnormal intensity ratio of L1₁(1 1 1) to L1₁(2 2 2) peak was

Figure 2. XRD θ -2 θ diffraction patterns for CoPt films deposited at various temperatures from RT to 750 °C at χ angles of 0° , 34.9° , and 55.1° .

obtained in Figure 2 due to the reduction of $L1_1(2\ 2\ 2)$ diffraction intensity. It is because the CoPt film is highly $(1\ 1\ 1)$ -textured, yielding a very strong $L1_1(2\ 2\ 2)$ peak. The $L1_1(2\ 2\ 2)$ peak intensity was substantially reduced using the shielding sheets to protect the photon detector against the damage from overshoot signals. In contrast, the intensity of the $L1_1(1\ 1\ 1)$ peak is much weaker. No reduction was required. The $L1_1(1\ 1\ 1)$ peak is quite broad with a full width at half maximum (FWHM) of 2.04° . Three fundamental peaks remained but their intensities were lower than those of the film with $T_s = 200^\circ\text{C}$. The $(0\ 0\ 1)$ and $(1\ 1\ 0)$ diffraction peaks of $L1_0$ CoPt are absent, revealing that the $L1_0$ CoPt phase is not formed. As T_s was increased to 300°C , the intensities of the $L1_1(1\ 1\ 1)$ and three fundamental peaks increased dramatically; the $L1_1(1\ 1\ 1)$ peak was broadened; the FWHM was as large as 5° . The highest $L1_1(1\ 1\ 1)$ peak was obtained at $T_s = 350^\circ\text{C}$ with the narrowest FWHM of 2.02° . Another superlattice peak of $L1_1(3\ 3\ 3)$ was present at $2\theta = 65.57^\circ$. All A1 peaks remained, although the intensities were lower than those of the film with $T_s = 300^\circ\text{C}$. When T_s reached 400°C , the $L1_1(1\ 1\ 1)$ peak was even lower and broader, whereas the intensities of the three fundamental peaks were higher again, suggesting that the A1 phase had gradually replaced the $L1_1$ phase. The A1 phase became predominant in the 500°C -grown sample and completely replaced the $L1_1$ phase at $T_s = 600^\circ\text{C}$. The improvement in crystal quality significantly increased the intensities of the fundamental peaks. The actual intensity of the peaks at $T_s \geq 600^\circ\text{C}$, shown in Figure 2, should be ten times higher because of the shielding of the raw signal. Notably, the diffraction peaks of $L1_1(1\ 1\ 1)$ are broad with a Lorentzian shape, similar to those obtained elsewhere [2–4], indicating the line broadening associated with a size effect in the epitaxially grown films. Size effects, including those associated with incoherently diffracting domains that are created by various planar defects such as dislocations, stacking faults, twins, anti-phase boundaries, grain boundaries and others, are believed to cause such line broadening [5].

The long-range order (LRO) parameter (S) of thin films with the $L1_1$ phase was measured. The structure factor of the $L1_1$ rhombohedral lattice, given by Lang et al. for the CuPt $L1_1$ structure, was adopted [6]: $F = 4\{[2X_{\text{Co}} + S(1 - 2X_{\text{Co}})]f_{\text{Co}} + [2X_{\text{Pt}} + S(1 - 2X_{\text{Pt}})]f_{\text{Pt}}\}$ if (hkl) are all even, and $F = 4S(f_{\text{Co}} - f_{\text{Pt}})$ if (hkl) are all odd, where X_{Pt} and X_{Co} are the atomic fractions, and f_{Pt} and f_{Co} are the atomic scattering factors of Pt and Co, respectively. In terms of F and intensities of the fundamental and superlattice diffractions, the LRO can be written as

$$S = \frac{(f_{\text{Pt}} + f_{\text{Cu}})}{(f_{\text{Pt}} - f_{\text{Cu}})} \sqrt{\frac{|c_{\text{F}}I_{\text{S}}|}{|c_{\text{S}}I_{\text{F}}|}} \quad (1)$$

where I_{S} and I_{F} are the intensities of the superlattice and fundamental diffractions obtained by integrating the Gaussian-fitted peak area. The correction parameters for the superlattice and fundamental peaks are c_{S} and c_{F} , respectively, which includes the corrections of Debye–Waller factor for room temperature, Lorentz-polarization factor, multiplicity, and absorption. Unlike that of the $L1_0$ structure, the fundamental reflection from the

$L1_1$ phase is obtained only for the exact stoichiometry of $\text{Co}_{50}\text{Pt}_{50}$, the structure factors of whose reflections with all even (hkl) are independent of S . The binary composition in this work is $\text{Co}_{48}\text{Pt}_{52}$, and so the extent of ordering is slightly overestimated. Nevertheless, all of the obtained S values are less than 0.4. The low S value may result from the residual A1 phase, because the $\text{A1}(1\ 1\ 1)$ peak overlaps the $L1_1(2\ 2\ 2)$ reflection, causing the intensity of the peak to be overestimated. The residual disordered phase also reduces the shrinkage of the lattice spacing along $[1\ 1\ 1]$ – only by about 0.3% by $L1_1$ ordering, the value of which is small compared to the 1.2% for the MBE-made films [2].

$L1_0$ ordering does not begin until T_s is increased to 700°C , as revealed by the presence of $(0\ 0\ 1)$ and $(1\ 1\ 0)$ peaks and asymmetric $(2\ 0\ 0)$ and $(2\ 2\ 0)$ peaks in Figure 2. The $(2\ 0\ 0)$ peak can be clearly separated into $L1_0(2\ 0\ 0)$, A1 $(2\ 0\ 0)$, and $L1_0(0\ 0\ 2)$ peaks by Gaussian fitting, yielding the order parameters [7]. The value of S calculated from the integrated areas under the $(0\ 0\ 1)$ and $(0\ 0\ 2)$ peaks is around 0.41. Visokay et al. [8] found that the $L1_0$ structure of CoPt that is deposited on $\text{MgO}(1\ 0\ 0)$ substrates forms at a growth temperature of 520°C . Their experiment was repeated herein for comparison. Additionally, $L1_0$ ordering was found to occur at 400°C in the sputter system. A 300°C difference in $L1_0$ ordering temperature was obtained. This difference may have resulted from the appearance of metastable $L1_1$ phase and the different strain energies induced by the lattice mismatch between CoPt films and $(2\ 0\ 0)$ or $(1\ 1\ 1)$ MgO substrates. As T_s was increased to 750°C , the superlattice peaks of $(0\ 0\ 1)$ and $(1\ 1\ 0)$ became narrow, with an FWHM of 0.4° , suggesting that the mean grain size increased. Clear splitting of $(2\ 0\ 0)$ and $(2\ 2\ 0)$ peaks was also observed and S increased to 0.72. Iwata et al. [2] concluded that the $L1_1$ phase was transformed into the AuCu-type structure ($L1_0$ phase) when the growth temperature was elevated above the temperature range for stability of the $L1_1$ phase. However, our investigation yielded different results. The structural analysis confirms that the structure of CoPt films that are deposited on $\text{MgO}(1\ 1\ 1)$ substrates at temperatures from RT to 750°C evolves in the sequence A1 (disordered) $\rightarrow L1_1 \rightarrow \text{A1} \rightarrow L1_0$. Therefore, when T_s is increased over a threshold temperature of 350°C , the ordered phase should be replaced by a disordered A1 phase rather than $L1_0$. After the film has become fully disordered, the $L1_0$ phase begins to form.

Figure 3 plots hysteresis loops of the samples for which results are presented in Figure 2. The longitudinal magnetization curve of the RT-deposited film is above the perpendicular one, suggesting in-plane anisotropy, which is a typical feature that arises from shape anisotropy for soft magnetic thin films. The film deposited at 200°C exhibits similar in-plane and out-of-plane hysteresis loops, implying that the nucleation of $L1_1$ phase onsets at 200°C . The perpendicular MCA is comparable to the shape anisotropy. However, this onset of $L1_1$ ordering cannot be determined simply from the structure identification. Substantial out-of-plane anisotropy was observed when T_s was between 250 and 400°C , confirming the formation of the $L1_1$ phase, as indicated in Figure 2. The film was perpendicularly saturated at an applied

Figure 3. Longitudinal and perpendicular hysteresis loops for CoPt films deposited at various temperatures from RT to 750 °C.

field of as low as 80 kA m^{-1} while longitudinal saturation in the longitudinal direction required a field of larger than 1.6 MA m^{-1} . The maximum anisotropy field (H_k) of 3.18 MA m^{-1} , was obtained at 4 K in the film that was grown at 300 °C. K_u , as determined from the area between the longitudinal and perpendicular magnetization curves, which was approximately $3.2 \times 10^5 \text{ J m}^{-3}$ —smaller than that obtained for the MBE sample ($2 \times 10^6 \text{ J m}^{-3}$). Low ordering ($S < 0.4$) is responsible for the low K_u . The saturated magnetization of the films is about 0.93 wb m^{-2} . The value is independent of the development of the L_{11} phase. This value is close to those of the disordered samples ($T_s = \text{RT}$, 200, and 600 °C), consistent with the theoretical calculations of Uba et al. [9]. The L_{11} films have a low remanence of under 0.125 wb m^{-2} . Similar results have been obtained for FePt and CoPt epitaxial films with continuous morphology [10,11]. The magnetization declines rapidly before the applied field is ramped from saturation to zero. The sharp magnetic reversal is related to the spontaneous nucleation of oppositely magnetized domains, as was predicted by Kittel [12]. Such hysteresis behavior is an indication of low impedance to domain wall motion, because of the low density of pinning sites in the perpendicular films. It also results in a low coercivity of below 39.8 kA m^{-1} . When T_s was increased to 500 °C, the perpendicular anisotropy is reduced by the competition from the shape anisotropy, which arises from the decreased amount of the L_{11} phase, and the perpendicular MCA which arises from the decreasing amount of the L_{11} phase, as evidenced by the structural data in Figure 2. The in-plane and out-of-plane hysteresis loops are identical to those of the film grown at 200 °C. The easy-axis of the film is rotated to the in-plane direction in the sample with $T_s = 600$ °C; shape anisotropy dominates the magnetic properties of the film by magnetic softening. As T_s reached 700 °C, the coercivity (H_c) was enhanced and the magnetization reduced due to the onset of L_{10} ordering. The H_c values of the in-plane and out-of-plane loops were 199 kA m^{-1} and 233 kA m^{-1} , respectively. The low ordering ($S = 0.41$) caused the film to continue to exhibit in-plane anisotropy. At $T_s = 750$ °C, H_c was greatly increased to 398 kA m^{-1} and the magnetization at the applied field of 1.6 MA m^{-1} ($M_{1.6\text{MA}}$) was reduced to 0.70 – 0.73 wb m^{-2} for M – H loops that had been measured in both directions. Similar H_c values and reduced $M_{1.6\text{MA}}$ in both directions have been found indicating the easy-

axis is tilted away from the normal direction. This is a typical feature of a (1 1 1)-textured CoPt L_{10} film.

In summary, the entire evolution of the structure and the magnetic properties of CoPt thin films with a metastable L_{11} structure were presented. The L_{11} phase is nucleated in the Al matrix at a growth temperature of 200 °C, develops gradually as the temperature is increased from 250 to 350 °C, and falls as T_s increases above 350 °C, transforming completely into Al at 600 °C. The formation of the L_{11} phase causes high perpendicular magnetic anisotropy. A maximum perpendicular H_k of 3.18 MA m^{-1} was obtained at 4 K for the L_{11} film grown at 300 °C. L_{10} ordering occurs at 700 °C, causing isotropic magnetic hardening due to the perfection of the (1 1 1) texture. Although the film contains a considerable amount of the residual disordered Al phase and planar defects, the L_{11} phase exhibits great potential in recording applications because of its perpendicular anisotropy and relatively low temperature of formation.

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