Structure Characterization of FePd, FePt, and CoPt Alloy Thin Films 
Epitaxially Grown on SrTiO₃(001) Single-Crystal Substrates

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FePd, FePt, and CoPt alloy epitaxial thin films are prepared on SrTiO₃(001) single-crystal substrates at 600 °C by using an ultra-high vacuum radio-frequency magnetron sputtering system. L₁₀ ordered phase formation is recognized for these films. The FePd film consists of L₁₀(001) single-crystal with the c-axis perpendicular to the substrate surface, whereas the FePt and the CoPt films involve two L₁₀(100) variants, whose c-axes are lying in-plane and rotated around the film normal by 90° each other, in addition to L₁₀(001) variant. A higher long-range order degree is observed in the order of FePd (0.61) > FePt (0.35) > CoPt (0.16). The FePd film shows a perpendicular magnetic anisotropy, while the FePt and the CoPt films show in-plane magnetic anisotropies. The magnetic property is influenced by the c-axis direction and the order degree.

Key words: FePd, FePt, CoPt, thin film, epitaxial growth, L₁₀ ordered phase, SrTiO₃(001) single-crystal substrate

1. Introduction

Perpendicular magnetic tunneling junctions have been investigated for magnetoresistive random access memory devices. Non-magnetic oxides such as MgO[1-5] and SrTiO₃[6,10-12] are used as an insulating layer material which is stacked between two ferromagnetic layers to form a magnetic tunneling junction (MTJ). For the magnetic layers, materials with high uniaxial magnetocrystalline anisotropy energy (Kₐ) are investigated[6-9]. The crystal structure of FePd, FePt, and CoPt alloys with the equiaxial composition varies between disordered (A₁) and ordered (L₁₀) structures. The L₁₀ ordered alloys have Kₐ greater than 10⁷ erg/cm³ along the c-axis direction[12]. The control of c-axis direction is an important issue as well as achieving a high order degree. The structural and magnetic properties of L₁₀ ordered FePd, FePt, and CoPt films formed on MgO(001)[6,9,11-19] and SrTiO₃(001)[15-21] have been investigated. In these previous works, L₁₀ ordering has been mainly estimated by out-of-plane X-ray diffraction (XRD). However, there is a possibility of L₁₀ crystal ordering with the c-axis lying in-plane in addition to the c-axis perpendicular orientation. Therefore, it is necessary to study the crystallographic structure by combination of out-of-plane and in-plane XRDs. For MTJ device applications of L₁₀ ordered magnetic material, it is important to find an optimized combination between magnetic and insulating materials where both an improved c-axis orientation and a high degree of ordering are realized. In our previous work[22], FePd, FePt, and CoPt films were prepared on MgO(001) substrates under similar experimental conditions to investigate the detailed crystal structure and the order degrees of resulting films. A higher order degree of L₁₀ structure and a well c-axis perpendicularly oriented film structure is realized for the combination of FePd magnetic material and MgO(001) substrate. As the SrTiO₃ material is another insulating layer candidate for realization of MTJ devices with high efficiency, it is interesting to investigate the structural properties of these kinds of magnetic material deposited on SrTiO₃(001) substrates. In the present study, FePd, FePt, and CoPt films are deposited on SrTiO₃(001) substrates under similar experimental conditions. The film growth process and the detailed crystal structure are studied for these films by using a reflection high-energy electron diffraction (RHEED) and XRDs with out-of-plane and in-plane modes. The film magnetic properties are measured and the relationship with the film structure is discussed.

2. Experimental procedure

FePd, FePt, and CoPt alloy films of 40 nm thickness were deposited on polished SrTiO₃(001) substrates at 600 °C by using a radio-frequency (RF) magnetron sputtering system equipped with 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 ultra-high vacuum chamber to obtain clean surfaces. Figure 1(a) shows the RHEED pattern observed for an FePd film on SrTiO₃(001) substrate after heating. A clear diffraction pattern corresponding to E₂(001) single-crystal surface shown in the schematic diagram of Fig. 2(a) is recognized. Fe₉₀Pd₅₀, Fe₅₀Pt₅₀, and Co₉₀Pt₁₀ (at. %) alloy targets of 3 inch diameter were employed. The distance between target and substrate was 150 mm. The Ar gas pressure during sputtering was kept constant at 0.67 Pa. The RF powers for FePd, FePt, and CoPt targets were respectively fixed at 35, 43, and 45 W, where the deposition rate was 0.02 nm/s for all materials. The film compositions were confirmed by energy dispersive X-ray spectroscopy and the errors were less than 4 at. % from the target compositions.

The surface structure was studied by RHEED. The resulting structure was investigated by 2θ/ω scan (out-of-plane) and 2θ/ϕ scan (in-plane) 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 A1 and L10 structures. In the present study, A1-based notation is applied to the L10 structure for simple comparison with the A1 structure.

3. Results and discussion

Figure 1(b-1) shows the RHEED pattern observed for an FePd film deposited on SrTiO3(001) substrate. A clear diffraction pattern consisting of only streaks is observed. An FePd epitaxial film is obtained on the substrate. The pattern corresponds to A1(001) [Figs. 2(b) or L10(001) [Fig. 2(c)]] single-crystal surface. When a streak pattern is observed, the identification of crystal structure is difficult, since the A1(001) and the L10(001) patterns are very similar. The crystal structure is thus determined by XRD.

Figures 3(a) and 4(a) show the out-of-plane and the in-plane XRD spectra, respectively. FePd(001) superlattice reflection is recognized in addition to FePd(002) fundamental reflection in the out-of-plane spectrum, whereas FePd(001) superlattice reflection is absent in the in-plane spectrum. The result shows that L10 ordered phase is formed in the film and that the film consists of L10(001) single-crystal with the c-axis perpendicular to the substrate surface. The epitaxial orientation relationship of FePd film with respect to SrTiO3 substrate is determined by RHEED and XRD as

\[ \text{FePd(001)[100]L10} \parallel \text{SrTiO3(001)[100]}. \] (type A)

Figures 1(c-1) and (d-1) show the RHEED patterns observed for FePt and CoPt films deposited on SrTiO3 substrates, respectively. Clear diffraction patterns are observed for both films. The FePt and the CoPt films are grown epitaxially on the substrates. Superlattice reflections corresponding to L10(100) crystal formation [Figs. 2(d), (e)] are recognized in the RHEED patterns, as shown by the arrows in the intensity profiles of Figs. 1(c-2) and (d-2). The films involve two L10(100) variants whose c-axes are lying in-plane and rotated around the film normal by 90° each other. Figures 3(b) and 4(b) show the XRD spectra. L10(001) superlattice reflections are observed in both the out-of-plane and the in-plane spectra. The FePt and the CoPt films consist of L10(001) variant mixed with L10(100) variants. The crystallographic orientation relationships are determined by RHEED and XRD as

\[ \text{FePt, CoPt(001)[100]L10} \parallel \text{SrTiO3(001)[100], (type A)} \]
\[ \text{FePt, CoPt(001)[010]L10} \parallel \text{SrTiO3(001)[100], (type B)} \]
\[ \text{FePt, CoPt(001)[001]L10} \parallel \text{SrTiO3(001)[100], (type B')} \]

The variant volume ratio is estimated from the XRD data. The integrated intensity (I) is proportional to structure (F), Lorentz-polarization (L), absorption (α), and temperature (T) factors20). The intensity ratio of L10(002)type A to L10(002)type λ and L10(200)type B or B' in out-of-plane reflection is thus given by

\[
\frac{I_{\text{L10(002)type A}}}{I_{\text{L10(002)type λ}}} = \frac{V(F^2LDA\text{L10(002)})}{V(F^2LDA\text{L10(002)}) + (1 - V)(F^2LDA\text{L10(200)})},
\]

where V (0 ≤ V ≤ 1) is the volume ratio of one L10(001) variant to L10 crystal, which consists of one L10(001) variant and two L10(100) variants, and the subscripts of L10(002) and L10(200) refer to the L10(002) and the L10(200) out-of-plane reflections, respectively. The [F_{\text{L10(002)}}^2] and [F_{\text{L10(200)}}^2] is given by

\[
|F_{\text{L10(002)}}|^2 = |F_{\text{L10(200)}}|^2 = (2(f_{\text{Fe or Co}} + f_{\text{Pt}}))^2,
\]

where \(f_{\text{Fe or Co}}\) and \(f_{\text{Pt}}\) are respectively the atomic
scattering factor of Fe or Co and Pt. Therefore, V is given by

$$V = \frac{I_{L10(002)} \cdot \text{LDA}_{L10(002)}}{I_{L10(002)b' = b(\text{LDA})}_{L10(002)} + I_{L10(002)b'' = b''(\text{LDA})}_{L10(002)}}.$$  \tag{3}

The volume ratios of $L10(001)_{\text{type A}} : L10(100)_{\text{type B}} : L10(100)_{\text{type B'}}$ for FePd, FePt, and CoPt films are calculated to be $[1 : 0 : 0]$, $[0.40 : 0.30 : 0.30]$, and $[0.48 : 0.26 : 0.26]$, respectively. The volume ratio of $L10(001)_{\text{type A}}$ variant is larger than those of $L10(100)_{\text{type B}}$ and $L10(100)_{\text{type B'}}$ variants for all materials. When the lattice mismatches between $L10$ magnetic crystal and SrTiO$_3$ substrate at the $L10(001)/\text{SrTiO}_3(001)$ and the $L10(100)/\text{SrTiO}_3(001)$ interfaces are compared, the mismatch along the $a'$-axis of $L10$ crystal is smaller than that along the $c$-axis for the three magnetic materials, as shown in Table 1. Therefore, $L10(001)$ crystal is considered to be preferentially formed on SrTiO$_3(001)$.

The long-range order degrees of $L10(001)_{\text{type A}}$ and $L10(100)_{\text{type B}}$ variants ($S_{\text{type A}}$ and $S_{\text{type B}}$) are calculated from the out-of-plane and the in-plane XRD data, respectively. The intensity ratio of $L10(001)$ to $L10(002)$ reflection is given by

$$\frac{I_{L10(001)}}{I_{L10(002)}} = \frac{[(F_{L10(001)} \cdot \text{LDA})_{L10(001)}]}{(F_{L10(002)} \cdot \text{LDA})_{L10(002)}}.$$ \tag{4}

The $|F_{L10(001)}|^2/|F_{L10(002)}|^2$ is calculated to be

$$\frac{|F_{L10(001)}|^2}{|F_{L10(002)}|^2} = \frac{2S_{\text{type A}}}{\{f(\text{Fe or Co} + \text{frd or Pr})\}^2}.$$ \tag{5}

The $S_{\text{type A}}$ or B is thus given by

$$S_{\text{type A or B}} = \frac{I_{L10(001)}((\text{Fe or Co} + \text{frd or Pr}))^2 (\text{LDA})_{L10(001)}}{I_{L10(002)}((\text{Fe or Co} + \text{frd or Pr}))^2 (\text{LDA})_{L10(002)}}.$$ \tag{6}

The total order degree ($S_{\text{total}}$) is expressed by

$$S_{\text{total}} = (S_{\text{type A}} + \frac{1}{2} (1 - V)S_{\text{type B}} + \frac{1}{2} (1 - V)S_{\text{type B'}}).$$ \tag{7}

The order degrees, ($S_{\text{type A}}$, $S_{\text{type B}}$, $S_{\text{total}}$), of FePd, FePt, and CoPt films are calculated to be 0.61, 0.61, (0.38, 0.33, 0.35), and (0.20, 0.11, 0.16), respectively. The order degrees are not so high when compared with those of polycrystalline films. The reason will be related with the difference of atomic diffusion in thin film. It is more enhanced in a polycrystalline film rather than in an epitaxial thin film because a larger amount of crystallographic defect such as crystal boundary promotes boundary diffusion within the film$^{241}$. Therefore, a higher degree of ordering tends to be observed for a polycrystalline thin film. A similar tendency of material dependence on $S$ is reported for films deposited on MgO(001) substrates$^{22}$. In order to promote $L10$ ordering for these alloy films, atomic diffusion is necessary. The atomic diffusion depends on the bonding energy between atoms which can be often related with the melting point. The melting point of FePd alloy is about 200°C lower than those of FePt and
FePd, FePt, and CoPt alloys. Therefore, the highest order degree is considered to be obtained for FePt film.

Figure 5 shows the magnetization curves. For the FePd/(001) L10 single-crystal film, a perpendicular magnetic anisotropy is observed and there are almost no differences in the in-plane hysteresis curves measured along SrTiO3[100] and SrTiO3[110]. The magnetic property is apparently reflecting the magnetocrystalline anisotropy of L10(001) crystal with the c-axis perpendicular to substrate surface. On the contrary, the FePt and the CoPt epitaxial films show in-plane magnetic anisotropies. This is due to the fact that the FePt and the CoPt films include L10(100) variants whose c-axes are lying in-plane in addition to L10(001) variant and due to that the S_{\text{type-A}} values of these films are not so high. For both films, the in-plane easy magnetization direction is observed along the SrTiO3[110], which is between the directions along the c-axes of the two L10(100) variants whose c-axes are lying in-plane. The result is similar to the case of hcp-Co film epitaxially grown on MgO(001) substrate with two (1120) variants whose c-axes are lying in-plane and rotated around film normal by 90° each other everywhere. The in-plane anisotropies of FePt and CoPt films are thus considered to be reflecting the magnetic properties of two L10 variants.

4. Conclusions

FePd, FePt, and CoPt epitaxial films are prepared on SrTiO3(001) substrates. L10 ordered films are obtained on the substrates for all materials. The FePd film consists of L10(001) crystal with the c-axis perpendicular to substrate surface. The FePt and the CoPt films involve two L10(100) variants with the c-axes parallel to substrate surface in addition to L10(001) variant. The volume ratios of [L10(001)_{\text{type-A}} : L10(100)_{\text{type-B}} : L10(100)_{\text{type-B'}}] observed for FePd, FePt, and CoPt films are [1 : 0 : 0], [0.40 : 0.30 : 0.30], and [0.48 : 0.26 : 0.26], respectively. L10(001) crystal is preferentially formed on SrTiO3(001) for all materials. A higher order degree of S_{\text{total}} is observed in the order of FePd (0.61) > FePt (0.35) > CoPt (0.16). The FePd film shows a perpendicular magnetic anisotropy, whereas the FePt and the CoPt films show in-plane magnetic anisotropies. The magnetic property is influenced by the c-axis direction and the order degree of L10 phase.

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References


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