Abnormal Enhancement of Ordered Phase in Sputter-Deposited (Fe_{1-x}Co_x)_{59}Pt_{41} Thin Films

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Magnetic (Fe_{1-x}Co_x)_{59}Pt_{41} alloy thin films have been sputter-deposited on Ti coated Si substrates. The surface morphologies of (Fe_{1-x}Co_x)_{59}Pt_{41} (x = 0.2, 0.4, 0.8) films changed with increasing Co content. The morphology variation was also correlated with phase transformation. An abnormal enhancement of ordered phase (L₀) has been identified at x = 0.2, as characterized by X-ray diffraction. Further increase of the Co content suppressed the disorder/order transformation. The abnormal enhancement of ordered phase also correlated to the morphologies of these alloy films. The formation of the order phase (at x = 0.2) increased the coercivity of the (Fe₀.₂Co₀.₈)₅₉Pt₄₁ thin films. The degree of ordering was also slightly enhanced. [doi:10.2320/matertrans.47.2086]

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1. Introduction

The magnetic properties of the materials are affected by factors including appropriate compositions, grain sizes, grain size distribution, and crystallographic matching between the underlayer and the magnetic layer.¹ The potential use of such materials for technological applications is however strongly dependent on their hysteresis properties, such as magnetization, remanence ratio, and coercivity. FeCo alloys have been studied widely because of the high saturation magnetization of up to approximately 1900 emu/cm³.²,³ However, the FeCo alloys exhibit only softened magnetic properties. In order to induce magnetic hardening, the chemistry of cubic crystalline FeCo alloys is varied by introducing Pt and Pd, which have been referred to in the literature as “nearly magnetic” metals, as their electron configurations are almost correct for a spontaneous magnetic moment.⁴ The large magnetocrystalline anisotropy of these alloys results from an anisotropic crystal structure (L₀ phase) and large spin-orbital interactions.⁵

For thin films of Fe-Pt systems, the crystal structure of a FePt film, deposited at room temperature, is typically a face-centered cubic fcc-FePt disordered phase, and exhibits soft magnetic behavior. This fcc-FePt phase can be transformed to hard magnetic face-centered-tetragonal (fct) L₁₀-FεPt ordered phase by annealing at high temperature.⁶,⁷ The fcc-FePt transforms to the L₁₀-phase, which has its c-axis slightly smaller than its a- and b-axis. The easy axis of the L₁₀-FePt phase is along the c-axis direction. L₁₀-FePt and L₁₀-CoPt exhibit a large magnetocrystalline anisotropy of 7 × 10⁶ and 4.9 × 10⁶ J/m³, respectively.⁸,⁹ This fact is important while discuss magnetic properties since coercivity is proportional to the crystalline anisotropy.¹⁰ In addition, the mechanism for high coercivity in FePt and CoPt polycrystalline alloy films has been proposed as magnetic domain wall pinning¹¹ at the ordered/disordered phase and c-axis variant ordered phase boundary.¹²

Due to the higher resistance of Co alloy thin films to chemical corrosion, larger magnetic coercivity, and a suitable exchange coupling,¹³ Fe-Co-Pt alloys are therefore of interest.

On the other hand, Watanabe and Masumoto¹⁴ reported remarkable permanent magnetic features of L₁₀-FePt bulk which was composed of more atomic ratio of Fe rather than equal stoichiometric Fe₅₀Pt₅₀. Another important factor, which may influence the magnetic properties of the magnetic thin films, is the underlayer. Wong et al.¹⁵ had shown that the degree of interfacial misfit is larger as the grain size is larger in Co films on Cr underlayers, which introduce stacking fault and misfit dislocation into the Co layer and the phase transformation is easier owing to the existence of these defects. The increase in the degree of order of FePt/Ti film is due to Ti underlayer introducing defects in the FePt layer will make the ordered transformation easier.¹⁶ However, very little studies on the Fe-Co-Pt thin films with L₁₀ phase have been found in literature.¹⁷ In the absence of any published thorough study of the effects of grain sizes and morphologies on magnetic properties of Fe-Co-Pt films. This work attempts to study magnetic characteristics by using Fe₅₀Pt₄₁ rather than Fe₅₀Pt₅₀. One set of alloys of interest is that in which 41 at% Pt is present and the Fe is partially replaced by Co. Using Ti underlayer along with the Co addition to investigate the phenomena of ordered/disordered phase transformation and the uniformity of grain size distribution, which are the two major factors influencing the performance of the magnetic films. Such films are interesting because the film property evolution during annealing takes place in three distinctive stages: initial nucleation of nanocrystallites, disorder/order transition, and grain growth and coalescence. The changes in the crystallinity, microstructures and the magnetic characteristics of these alloy films are also investigated.

2. Experimental Details

The (Fe₁₋ₓCoₓ)₅₉Pt₄₁ thin film system with thicknesses 150 nm was prepared by sputtering composite targets on
heated substrates using a d.c. sputtering system with pure Ar (99.9%) as sputter gas. The magnetic layers were sputtered onto Si substrates after the deposition of titanium underlayer with thicknesses of 20 nm. Targets were prepared by melting stoichiometric pure cobalt (99.99%) and iron (99.97%) to form the FeCo alloy in an r.f. furnace. During deposition, the substrate temperature was fixed at 573 K. The base pressure of the system was less than 6 × 10⁻⁵ Pa, and working pressure was 6.67 Pa. The growth rate of (Fe₁₋ₓCoₓ)₃₀Pt₄₁ thin film system was controlled at 2.5 nm s⁻¹ and iron (99.97%) to form the FeCo alloy in an r.f. furnace. During deposition, the substrate temperature was fixed at 573 K. The base pressure of the system was less than 6 × 10⁻⁵ Pa, and working pressure was 6.67 Pa. The growth rate of (Fe₁₋ₓCoₓ)₃₀Pt₄₁ thin film system was controlled at 2.5 nm s⁻¹ and the normal thickness was evaluated based on the sputtering time and micrograph of cross-section film. The structure and the magnetic properties of the films were observed as a function of post annealing temperatures (773–973 K). The crystal structures of the samples were characterized by multipurpose X-ray thin film diffractometry (XRD, Rigaku RINT 200). The surface composition and depth-profile analysis were obtained using an Auger electron spectroscopy (AES, 670 PHI Xi). The surface morphologies and film thickness were observed by field emission scanning electron microscopy (FE-SEM, Philips XL40). The lattice images of the thin film were obtained by transmission electron microscopy (TEM, Philips Tecnai G2 F20). A superconducting quantum interference device magnetometer (SQUID, Quantum Design MPMS7) was utilized to plot the hysteresis loops in magnetic fields of up to 30 kOe.

3. Results and Discussions

3.1 Crystallinity

Figure 1 shows XRD patterns of (Fe₁₋ₓCoₓ)₃₀Pt₄₁ thin films, with x = 0.0, 0.2, 0.4, 0.8, on Ti underlayer. The as-deposited (Fe₁₋ₓCoₓ)₃₀Pt₄₁ thin films tend to exhibit fcc structures matching those of fcc-FePt (JCPDS 29-0717). This disordered phase of (Fe₁₋ₓCoₓ)₃₀Pt₄₁ thin film is (111) textured, since the (111) plane is the most close-packed plane, which has lowest surface energy. As Co content increases, the (111) peaks shift to higher angles (Fig. 1). Considering the similar atomic radii Fe and Co (0.126 nm for Fe and 0.125 nm for Co), it is reasonable to assume that the Co atoms occupy the Fe sites in the lattices of the Fe₅₀Pt₄₁ alloys.

The XRD patterns of (Fe₁₋ₓCoₓ)₃₀Pt₄₁/Ti thin film with varied Co contents annealed at 873 K are shown in Fig. 2. The Fe₅₀Pt₄₁, (Fe₀.₈Co₂₀.₂)₃₀Pt₄₁ and (Fe₀.₆Co₂₀.₄)₃₀Pt₄₁ films show (001) and (110) superlattice peaks, which indicates existence of L₁₀ phase. The Fe₅₀Pt₄₁ film develops pronounced (111) texture and the (001) ordered L₁₀ phase also appears, but the characteristic (200) and (002) peaks were indistinguishable.

Interestingly, for the slightly doped (Fe₀.₈Co₀.₂)₃₀Pt₄₁ film, the original fcc (200) peak splits into fct (200) and fct (002) peaks. It is suggesting that the transformation is thermodynamically first order, occurring by nucleation and growth of the ordered phase in the disordered matrix. Compared with the un-doped Fe₅₀Pt₄₁, it suggests that the small amount of Co (12 at%, x = 0.2) in Fe₅₀Pt₄₁ enhances L₁₀ phase ordering process at annealing temperature of 873 K.

However, too high a Co content suppresses the ordering process. For the (Fe₁₋ₓCoₓ)₃₀Pt₄₁ film with x = 0.4, the fcc phase is predominant over the L₁₀ phase. Further increase of Co content, (Fe₀.₂Co₀.₈)₃₀Pt₄₁, results in only fcc phase, which indicates that the phase transition to the ordered phase has to be induced at a relatively higher temperature for high Co contented films. These results agree with recent study of Barmak et al., where the FePt showed a lower activation energy of transformation than CoPt. Interestingly, the slightly Co doped film (x = 0.2) shows an enhanced L₁₀ phase. This abnormal formation of L₁₀ phase may be attributed to the enhanced recrystallization, induced by the suitable Co content and the Ti underlayer. We have carried out the same experiments on different bare Si substrates, and the abnormal enhancement of L₁₀ phase was not observed. In addition, a strain existed in (Fe₀.₈Co₀.₂)₃₀Pt₄₁ films would bring about assistance in phase transformation. A small increase in the amount of Co (x = 0.2) can introduce a lattice distortion, i.e. strain, which enhanced the transformation of the disordered phase in (Fe₁₋ₓCoₓ)₃₀Pt₄₁ thin films to the ordered L₁₀ phase, owing to the existence of strain. The results agree with the first principle calculation by MacLaren et al., where abnormal anisotropy occurs at around 10 at% of Co doping in FePt alloys, or 10 at% of Fe in CoPt alloys.

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**Fig. 1** XRD patterns of the as-deposited (Fe₁₋ₓCoₓ)₃₀Pt₄₁/Ti (x = 0.0, 0.2, 0.4, 0.8) films. (d-spacing (111), d₁₁₁, are also indicated).

**Fig. 2** XRD patterns of (Fe₁₋ₓCoₓ)₃₀Pt₄₁/Ti films with different Co contentes post annealed at 873 K for 1 h. (a) x = 0, (b) x = 0.2, (c) x = 0.4, (d) x = 0.8.
The (Fe<sub>0.2</sub>Co<sub>0.8</sub>)<sub>59</sub>Pt<sub>41</sub>/Ti film annealed at a higher temperature of 973 K still does not transform to L<sub>10</sub> phase. It may be due to the diffusion of Ti underlayer. As shown in Fig. 3, severe inter-diffusion can be found at the (Fe<sub>0.2</sub>Co<sub>0.8</sub>)<sub>59</sub>Pt<sub>41</sub>/Ti interface. Significant inter-diffusion between Ti and ferromagnetic metals is well known. For example, XPS study of Ti/Co/Si multilayers annealed at 923 K indicated the presence of Ti at the Co/Si interface.<sup>21</sup> Meanwhile, the diffusivity of Co in Ti was estimated to be about 10<sup>-8</sup> (cm<sup>2</sup> s<sup>-1</sup>) at high temperature.<sup>22</sup> In alloy systems containing Co, Co diffuses rapidly into the Ti layer, forming a Co-Ti solid solution. Since the solubility of Co in Ti is finite, excess Co atoms in the Co-Ti solid solution diffuse further into the Si substrate. As a consequence, the suppression of L<sub>10</sub> phase in high Co contented thin films may be attributed to the higher ordering temperatures and Ti/Co inter-diffusion.

3.2 Microstructures

The grain sizes of Fe<sub>59</sub>Pt<sub>41</sub> and (Fe<sub>0.8</sub>Co<sub>0.2</sub>)<sub>59</sub>Pt<sub>41</sub> was calculated from Scherrer equation, which were 75 nm and 60 nm, respectively. Figure 4 shows the surface morphologies of as-deposited (Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>59</sub>Pt<sub>41</sub>/Ti films with different Co contents (x = 0, 0.2, 0.4, 0.8). Without Co, the grain size of the Fe<sub>59</sub>Pt<sub>41</sub> film is as small as 10 nm and the grain size distribution is very uniform. The surface morphological contrast becomes more obvious with Co dopings (Figs. 4(b)–4(d)). For the (Fe<sub>0.8</sub>Co<sub>0.2</sub>)<sub>59</sub>Pt<sub>41</sub> film, the grain sizes are about 20 nm. At x = 0.4, the grain sizes slightly increase. Further increase of the Co content to x = 0.8, the grain sizes increase to about 30 nm.

The average grain size variation depends on the annealing temperatures and the compositions, as shown in Fig. 5. There is significant increase in average grain size upon annealing at 773 K, for the Fe<sub>59</sub>Pt<sub>41</sub> films. The grain sizes further increase as annealed at temperatures beyond 873 K. For the Co doped samples, grain variation is less significant. The influence of annealing temperature on grain size becomes minor at higher Co contents. It can be observed that samples of Fe<sub>59</sub>Pt<sub>41</sub> and low Co contented (Fe<sub>0.8</sub>Co<sub>0.2</sub>)<sub>59</sub>Pt<sub>41</sub> show more obvious recrystallization and grain growth, which may correlate to the formation of L<sub>10</sub> phase as shown in Fig. 2. Comparing films with different Co additives annealed at 873 K (Figs. 6(a)–6(d)), the Fe<sub>59</sub>Pt<sub>41</sub> grains coalesce to form larger grains and the surface morphological contrast becomes more blurred (Fig. 6(a)). In the (Fe<sub>0.8</sub>Co<sub>0.2</sub>)<sub>59</sub>Pt<sub>41</sub> film, the distribution of grain size becomes very homogeneous. In addition, the cross-sectional image of (Fe<sub>0.8</sub>Co<sub>0.2</sub>)<sub>59</sub>Pt<sub>41</sub>/Ti films (Fig. 7) illustrates that every individual grain is clearly isolated from each
other. It implies that the surface morphology is changed by adding Co.

However the films containing higher amounts of Co, (Fe$_{0.2}$Co$_{0.8}$)$_{59}$Pt$_{41}$, were not as susceptible to coalescing. Toney et al. proposed that the Fe$_{59}$Pt$_{41}$ grains coalesce to form larger grains. It is due to the formation of the L1$_0$ phase by nucleation and growth; once this phase forms, it grows quickly (since it is thermodynamically stable), while the untransformed fcc part of the film does not grow significantly. Therefore, high Co additive in the (Fe$_{1-x}$Co$_{x}$)$_{59}$Pt$_{41}$ films prevent morphologies from coalescing with the Co. As shown in the XRD patterns (Fig. 2), high Co contented thin films exhibit less significant L1$_0$ phase, indicating a higher nucleation barrier to the formation of the L1$_0$ phase. In contrast, the grain size of fcc (untransformed) phase is much smaller than that of the L1$_0$ phase, and is not susceptible to increased temperature. Therefore the (Fe$_{0.2}$Co$_{0.8}$)$_{59}$Pt$_{41}$ film maintains small grain size comparing to those of Fe$_{59}$Pt$_{41}$.

These results are in agreement with a recent paper by Chen, et al. which reported that Fe-Co-Pt nanocrystals with higher Co contents exhibited smaller crystallite sizes than those containing lower amounts of Co, after annealing at 973 K for one hour.

### 3.3 Magnetic properties

Magnetic hysteresis curves were measured on a SQUID using an out of plane 30 kOe saturating field. Since only the 873 K annealed Fe$_{41}$Pt$_{59}$ and (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$ samples exhibit appreciable ordered phase, the magnetic hysteresis curves of these films are compared in Fig. 8. The magnetic properties, such as coercivity, Hc, ordering parameters, S, saturation magnetization, Ms, remanence ratio, Mr/ Ms, and energy product, BH$_{max}$, of (Fe$_{1-x}$Co$_{x}$)$_{59}$Pt$_{41}$/Ti films with different Co contents (x = 0, 0.2, 0.4, 0.8) are summarized in Table 1. The Ms of Fe$_{41}$Pt$_{59}$ film is about 1012 emu/cm$^3$, which is higher than that of (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$, 910 emu/cm$^3$. However, the sample (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$ exhibits a high ordering parameter of 0.78. This decrease in Ms values of (Fe$_{1-x}$Co$_{x}$)$_{59}$Pt$_{41}$ films with small amount of Co doping (x = 0.2) is mainly due to the increase of L1$_0$ phase content in the film, because the Ms value of fcc phase is higher than that of L1$_0$ phase. For this reason, the Ms values of alloy films with high Co concentrations are between 1100 to 1200 emu/cm$^3$. Because microstructures of Fe$_{59}$Pt$_{41}$ film reveals grain coalesces which leads to the increased strong exchange coupling, the remanence ratio of Fe$_{59}$Pt$_{41}$ was higher than that of (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$. The strengthened granular interaction permits narrower transition widths in magnetization process, which reveals a higher maintenance of square loop for magnetic Fe$_{59}$Pt$_{41}$ film. While at the Co content above x = 0.8, grains consisting of a disordered phase and distinct grain boundary result in weak exchange coupling force and bring about a lowest remanence ratio (Table 1).

There is a strong correlation between S and Hc. The ordering parameters measured from XRD patterns show an S value of 0.66 and 0.78 for Fe$_{59}$Pt$_{41}$ and (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$ film, respectively. The S value decreases to 0.4 for x = 0.4. At x = 0.8, the ordering parameter approaches zero due to too high of Co content. The Hc of (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$ film is as high as about 6 kOe, indicating a higher degree of ordering. It is due to a small increase of Co, which enhances the ability of the (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$ to transform to the ordered L1$_0$ phase.

### Table 1

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<th>Composition, x</th>
<th>Hc / Oe</th>
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<th>Ms / emu-cm$^3$</th>
<th>Mr/Ms</th>
<th>BH$_{max}$/MOe</th>
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Fig. 8 Hysteresis loops measured in out of plane magnetic field for the Fe$_{59}$Pt$_{41}$ and (Fe$_{0.8}$Co$_{0.2}$)$_{59}$Pt$_{41}$ alloy films annealed at 873 K for 1 h.
pinning sites that impede domain-wall motion and cause high magnetic hardening in the \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) film. TEM results verified some planar defects of twins in the \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) film. The TEM bright-field image in Fig. 9(a) shows a plane view of the \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) film. Figure 9(b) magnifies the twins in a single grain. The twin structures were formed by nucleation and growth of ordered regions due to slight Co additive introducing elastic energy.

For \(\text{Fe}_{59}\text{Pt}_{41}\) film, the inter-granular exchange coupling caused by extreme aggregation of grains is adequate to give a high remanence ratio and energy product. However, excessive exchange coupling leads to the decrease of the coercivity. Thus, the \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) films with the \(L1_0\) phase possessed a higher the coercivity than that of \(\text{Fe}_{59}\text{Pt}_{41}\).

Considering both films of \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) and \(\text{(Fe}_{0.2}\text{-Co}_{0.8})_{29}\text{Pt}_{41}\) have small ordered parameters, the Hc values drastically decrease. It indicates that higher temperature is needed for ordered phase formation.

4. Conclusions

Utilizing DC sputtering, magnetic \(\text{(Fe}_{1-x}\text{Co})_{29}\text{Pt}_{41}\) \((0.0, 0.2, 0.4, 0.8)\) thin films were deposited on Ti coated Si substrates. Initial nucleation of disordered fcc nanocrystals occurs in the as-deposited alloy films. The disorder/order transition is induced by the elevated temperature during annealing. An abnormal enhanced ordered \(L1_0\) phase has been observed in \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) films. This phenomenon may be attributed to the enhanced recrystallization, induced by the suitable Co content and the Ti underlayer. Further increasing the Co contents suppresses this transformation. The surface morphology is changed by adding Co. However the morphologies of the films containing higher amounts of Co are less susceptible to annealing temperature. Therefore the microstructures of \(\text{(Fe}_{1-x}\text{Co})_{29}\text{Pt}_{41}/\text{Ti}\) films are controlled by Co additives rather than the Ti underlayer. The magnetic properties of the films have been measured. The \(M_s\) of \(\text{Fe}_{59}\text{Pt}_{41}\) film is higher than that of \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\), mainly due to the enhanced \(L1_0\) phase in the \(\text{(Fe}_{0.8}\text{-Co}_{0.2})_{29}\text{Pt}_{41}\) film. The coercivity of the \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) film is influenced by degree of ordering and exchange coupling in the alloy films. Therefore, the \(\text{(Fe}_{0.8}\text{Co}_{0.2})_{29}\text{Pt}_{41}\) film possesses a relatively higher Hc value of about 6 kOe.

Acknowledgments

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References