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## Low-temperature ordering of L1<sub>0</sub>-CoPt thin films promoted by Sn, Pb, Sb, and Bi additives

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We have studied the effect of additional elements of Sn, Pb, Sb, and Bi on the ordering of L1<sub>0</sub>-CoPt films. All of these additives are demonstrated to be very effective to promote the ordering and developing of a very large coercivity of the samples annealed at 400 °C. It is worth noting that this annealing temperature for ordering is 200 °C lower than that of pure CoPt. The crystallographic and chemical analyses have revealed that these additives easily diffuse and segregate onto the film surfaces by postannealing because of their very low surface free energy and extremely low solubility in Co. Therefore, it seems reasonable to conclude that the ordering in the CoPt film is significantly promoted at much lower temperature by the aid of a lot of defects produced by the additives excreted by postannealing. © 2001 American Institute of Physics. [DOI: 10.1063/1.1346628]

Magnetic recording is a predominant data storage technology and continues to make rapid advances in data densities. In the near future, however, achievable data densities will be restricted by fundamental physical phenomena such as bit instability due to superparamagnetism. Equiatomic Co- and Fe-Pt alloy films with an L1<sub>0</sub>-ordered structure have been attractive as ultrahigh-density magnetic recording media,<sup>1,2</sup> because the thermal agitation of spins would be suppressed due to their very large magnetic anisotropy with a level of 10<sup>7</sup>-10<sup>8</sup> erg/cc.<sup>3,4</sup> In general, however, high temperature processes above 600 °C are indispensable for ordering in CoPt and FePt.<sup>5-8</sup> From a practical viewpoint, such high temperature processes are unsuitable for mass-productions of magnetic recording media. There have been a few attempts to reduce the temperature for ordering. Artymowicz *et al.* studied a formation of ordered L1<sub>0</sub>-CoPt from epitaxial Pt/Co multilayers<sup>9</sup> and found that the activation energy ( $E_a$ ) for the ordering can be decreased down to 2.1 eV, significantly lower than the activation energies for the self-diffusion of Pt ( $E_a=2.91$  eV) and  $\beta$ -Co ( $E_a=2.89$  eV). They declared that the reasons for this lower energy are gradient-assisted diffusion and large chemical diffusivity of Co in Pt. This result indicates a significance of diffusion to the ordering. Recently the present authors found that an addition of Ag into CoPt/SiO<sub>2</sub> granular films promotes a disorder/order transformation, resulting in an appreciable reduction of the temperature for ordering.<sup>10</sup> From the Arrhenius plots of the order parameter  $S$  as a function of inverse of annealing temperature  $1/T$ , the activation energy for the ordering was found to decrease from 2.7 to 2.4 eV by addition of 5 at. % Ag.<sup>11</sup> Since Ag is almost immiscible with Co in an equilibrium state,<sup>12</sup> it would precipitate as clusters in CoPt

by annealing if the atomic interaction energy of Ag-Pt is higher than that of Co-Pt. In fact, Ag precipitation in annealed CoPt-Ag/SiO<sub>2</sub> granular films was clearly observed by x-ray diffraction.<sup>11</sup> Surface segregation of Ag may also promote the interdiffusion of Co and Pt, because the surface energy of Ag ( $\gamma=1.30$  Jm<sup>-2</sup> at 298 K) is lower than that of Co (2.71 Jm<sup>-2</sup>) and Pt (2.69 Jm<sup>-2</sup>).<sup>13</sup>

In this letter, we show the effects of the additional elements such as Sn, Pb, Sb, and Bi on the ordering in equiatomic CoPt films. All these elements were selected because of their extremely low solubility in Co along with their low surface free energy.

The Co<sub>0.45</sub>Pt<sub>0.55</sub>-M (M=Sn, Pb, Sb, Bi, and Ag) films were prepared on fused quartz substrates in a rf sputtering system under an argon gas pressure of 5 mTorr at a substrate temperature of 100 °C. A CoPt target with M chips placed uniformly on it was used. The film thickness was fixed at 40 nm, and the deposition rate was 2 nm/min. Annealing was performed in a vacuum chamber of 5 × 10<sup>-7</sup> Torr at the temperature of 25-650 °C for 1 h. The crystal structures were identified by x-ray diffractometry with Cu K $\alpha$  radiation. The film compositions were determined by energy dispersive x-ray and x-ray photoelectron spectroscopies. The room temperature magnetic properties were measured with a vibrating sample magnetometer in a maximum field of 10 kOe.

Figure 1 shows the variation of in-plane coercivity  $H_c$  for CoPt- $x$  at. % M (M=Sn, Pb, Sb, Bi, and Ag) films as functions of annealing temperature  $T_a$ . It is obvious that the addition of M significantly lowers the annealing temperature necessary for a high  $H_c$ . Especially, in the case of M=Sb,  $T_a \sim 400$  °C is enough high to increase  $H_c$  above 5 kOe. The temperature of  $T_a$  necessary for such a high coercivity is much lower, compared with that of pure CoPt. Note that a higher temperature annealing above 600 °C is required for a

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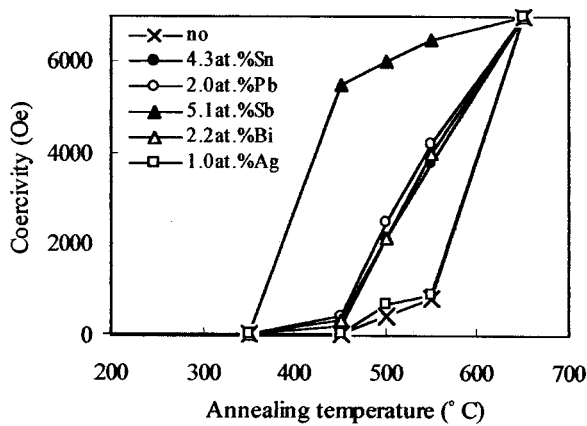


FIG. 1. Variation of in-plane coercivity  $H_c$  for 40 nm thick CoPt-M (M=Sn, Pb, Sb, Bi, Ag) films as a function of annealing temperature. Note that the external field of 10 kOe was insufficient for saturation for the samples with  $H_c \geq 5$  kOe.

partial ordering and a high  $H_c$  for pure CoPt. Such a remarkable additive effect on the magnetic properties can be understood from the x-ray diffraction scans shown in Figs. 2(a) and 2(b). For M=Pb in Fig. 2(a), very weak superstructure lines 001 and 110 from the ordered  $L1_0$ -CoPt appear at  $T_a = 500^\circ\text{C}$ , indicating that a partial ordering starts to occur around this temperature. More enhanced ordering can be achieved in CoPt 5.1at.% Sb [Fig. 2(b)] even at  $T_a = 450^\circ\text{C}$ , developing a very large coercivity as high as 5.5 kOe, as shown in Fig. 3.

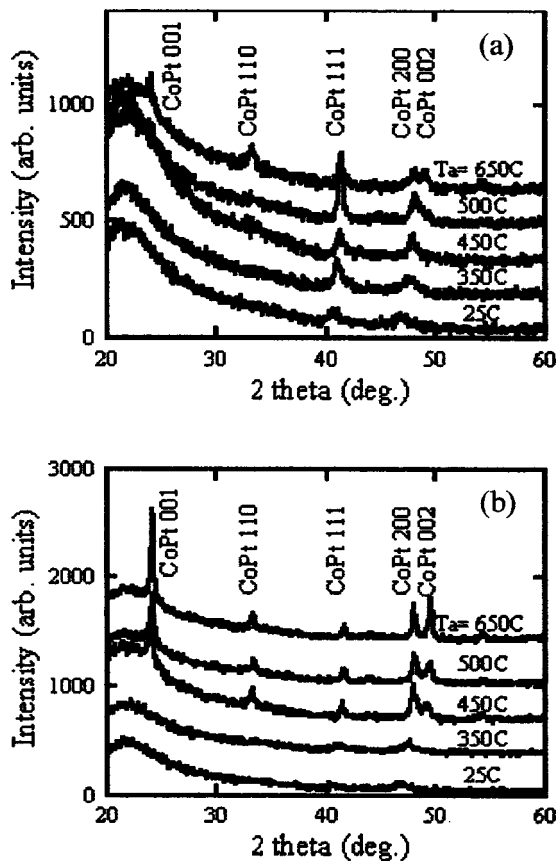


FIG. 2. Typical  $\theta$ - $2\theta$  scans of 40 nm thick (a) CoPt 2.0at.% Pb and (b) CoPt 5.1at.% Sb films as a function of annealing temperature  $T_a$ . Note that strong superstructure lines 001 and 110 from the ordered  $L1_0$ -CoPt are observed in the data on the CoPt-Sb film.

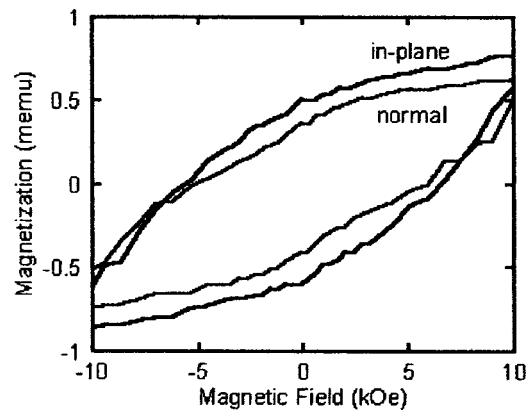


FIG. 3. In-plane and out-of-plane magnetization curves of a 40 nm thick CoPt 5.1at.% Sb film annealed at  $T_a = 450^\circ\text{C}$ .

As mentioned above, the addition of Sb is found to be very effective to promote the ordering of CoPt. For the other additives Sn, Pb, and Bi, a significant reduction of the annealing temperature for ordering can also be realized with increasing concentration of the additional elements M. Figures 4(a) and 4(b), respectively, show the concentration dependence of coercivity. In contrast with CoPt/SiO<sub>2</sub> granular films,<sup>10</sup> Ag gives no effect on the ordering, although the reason is not yet clear. Although the optimal quantity for ordering depends on M, for all additives except Ag examined in the present work, the increase of  $x$  gives rise to a significant reduction of the temperature for ordering, accompanied by a rapid increase in coercivity. In order to investigate the role of M in CoPt, we traced variation of the lattice spacing  $d_{111}$  of CoPt-M as a function of annealing temperature. It is clearly noticed in Fig. 5(a) that the variation of  $d_{111}$  for CoPt-Pb and -Bi is in agreement with that of pure CoPt. This result indicates that Pb and Bi atoms are not incorpo-

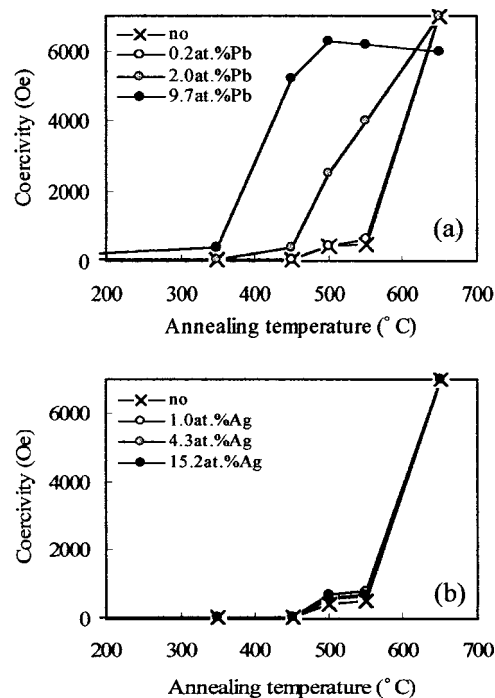


FIG. 4. In-plane coercivity vs annealing temperature for 40 nm thick (a) CoPt-Pb and (b) CoPt-Ag films as a function of concentration of the additional Pb and Ag.

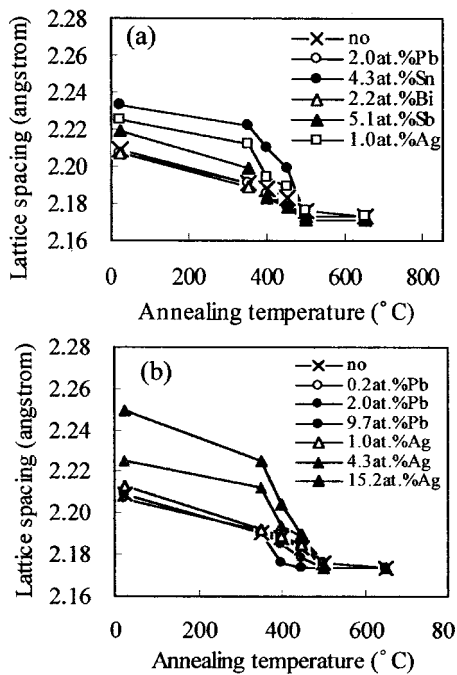


FIG. 5. Lattice spacing  $d_{111}$  of CoPt vs annealing temperature for 40 nm thick (a) CoPt-M films (M=Sn, Pb, Sb, Bi, Ag) and (b) CoPt- $x$  at.% M (M=Pb, Ag) films.

rated in the crystal lattice of CoPt because of their very large atomic radii compared with those of Co and Pt.<sup>14</sup> For M=Sn, Sb, and Ag, CoPt lattices are appreciably expanded in as-deposited states and are rapidly decreased by post-annealing, indicating that these additives form a solid solution with CoPt due to their smaller atomic radii compared with those of Pb and Bi. Formation of such CoPt-Sn, -Sb, and -Ag solid solutions has been confirmed by investigating the dependence of  $d_{111}$  on the additive concentration  $x$ . In Fig. 5(b), we show the variation of  $d_{111}$  against  $x$  for CoPt-Ag and -Pb films. It is noted that Pb concentration gives no effect on  $d_{111}$  of the as-deposited CoPt films. In contrast, the increase of Ag concentration gives rise to a monotonic expansion of the CoPt lattice due to formation of a solid solution. It is clearly noticed from Figs. 5(a) and 5(b) that the lattice spacing of CoPt-Sn, -Sb, and -Ag decreases very rapidly around  $T_a \sim 400^\circ\text{C}$  and approaches the value of pure CoPt, showing that all these supersaturated atoms are easily excreted from the CoPt lattice due to an out diffusion.

All the additives examined in the present work are easily diffused by low temperature annealing, and would precipitate in the films or segregate onto the film surfaces. In order to investigate this point, we have measured the compositional depth profiles of as-made and annealed CoPt 5.1at.% Sb films. Figures 6(a) and 6(b), respectively, show the Auger electron spectroscopy depth profiles of the CoPt-5.1at.% Sb films before and after annealing at  $650^\circ\text{C}$ . It is clearly confirmed that Sb tends to diffuse toward the film surfaces. Such a surface segregation is caused by both a very low surface free energy of the additives and an extremely limited solubility in Co. It is also found that, in the case of CoPt-Pb, Pb is entirely excreted from the film and sublimated due to its high vapor pressure when annealing temperature is above  $650^\circ\text{C}$ . Therefore, we reasonably conclude that the reduc-

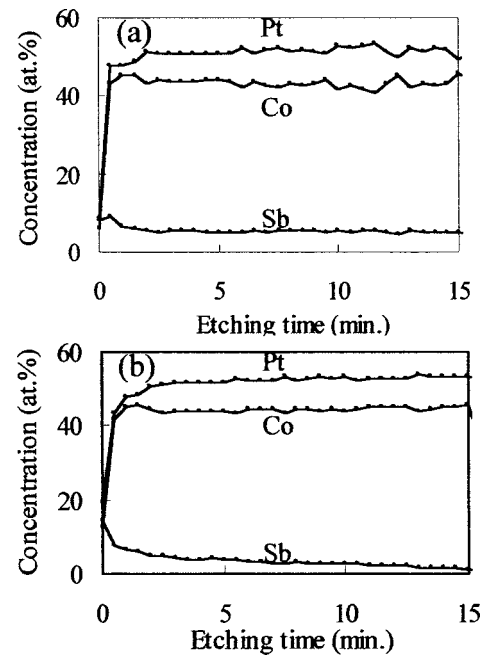


FIG. 6. Compositional depth profiles for (a) as-made and (b) annealed 40 nm thick CoPt 5.1at.% Pb films. Etching rate is about 2.2 nm/min.

tion of the temperature for ordering of CoPt is promoted by the aid of a lot of defects produced by the additives excreted by annealing.

In summary we have found that the annealing temperature for ordering of L1<sub>0</sub>-CoPt can be significantly lowered down to  $T_a \sim 400^\circ\text{C}$  by addition of Sn, Pb, Sb, and Bi. This remarkable reduction of the annealing temperature is closely related to large diffusivities of Co and Pt associated with defects caused by the excreted additives.

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