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Effects of Annealing Pressures on the Ordering and Microstructures of FePt:Ag Nanocomposite Films

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FePt:Ag (100 nm) nanocomposite thin films were prepared on naturally-oxidized Si substrates by dc magnetron sputtering at room temperature. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are used to investigate the effects of annealing pressures on the ordering processes and microstructures of these films. The average sizes for the $L1_0$ ordered domains and the FePt grains are reduced to $d = 9$ nm and $D = 13$ nm from $d = 19$ nm and $D = 34$ nm, respectively, when the annealing pressure is enhanced to 0.6 GPa from room pressure at 873 K. Furthermore, the size distribution is improved into a narrow range. With increasing pressure, the coercivity of $L1_0$-FePt:Ag thin films decreases from 15.1 to 7.6 kOe. In the present study, the effects of high pressure on the $L1_0$ ordering processes and microstructures of FePt:Ag nanocomposite films were discussed.

Keywords : FePt, nanocomposite films, high pressure, ordering

1. Introduction

Equiatomic FePt particle films with an $L1_0$ ordered structure, a small grain size, a (00l) texture and isolated by nonmagnetic matrix are potential candidates for ultra-high density magnetic recording media [1-3]. Though much progress has been made on the simultaneous control of the small grain size, nonmagnetic matrix isolation and (00l) texture [4-6], the transition temperature from the disordered face-centered-cubic structure (i.e., $A1$ structure) to the ordered $L1_0$ structure of the FePt particle films with the above ideal structures are too high for their practical application [7-9]. And with the decrease of the grain size, the ordering temperatures of the FePt particle films become higher [10, 11]. To reduce the ordering temperature of the FePt particle films, understanding the character and physical mechanism for the Fe and Pt atomic migration during the ordering process are of great importance and interest since the ordering of the FePt thin film is controlled by the atomic diffusion. It was demonstrated that the atomic diffusion behavior for the structural phase transitions can be directly understood by the activation volume usually determined from structural parameters measurements at different pressures [12, 13]. It is required that the structural transition parameters such as the grain size and transition degree are very sensitive to the variety of the annealing pressures and the effects of the annealing pressures on the structural transition are required to be made clear. Though the effects of the annealing pressures on the ordering of the single FePt continuous films have been reported in our previous works [14], the effects of the pressures on the ordering of the FePt particle films are not clear. Therefore, in this paper, we choose a typical FePt: Ag nanocomposite particle film system and in detail study the effects of the annealing pressures on the ordering and microstructure of the FePt:Ag particle films. It is demonstrated that both the size of the $L1_0$ ordered domains and the grains of FePt: Ag films are obviously reduced by the high pressure and the size distribution is improved. The ordering degree of the FePt: Ag nanocomposite film is reduced by the high pressure. The studies of this paper reveal that the ordering process of FePt Ag particle films is obviously sensitive to the annealing pressures and thus open the door for the study of the character and physical mechanism of the atomic migration during the FePt ordering process, which is of great importance for understanding the ordering process and reducing the ordering temperatures of FePt particle films.

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2. Experiments

$(Fe_{51}Pt_{49})_{90}Ag_{10}$ (named as FePt:Ag below) thin films with a thickness of ~100 nm were deposited on natively oxidized Si (100) substrates by magnetron sputtering from a binary $Fe_{50}Pt_{50}$ alloy target on which some little Ag sheets were placed at an argon pressure of 6.0 Pa at room temperature. The as-deposited FePt:Ag films were annealed under pressures up to 0.6 GPa at a temperature of 873 K for 30 min by employing a Gleeble-3500 hot-pressure simulator with a vacuum chamber ($p < 10^{-3}$ Pa). The experimental details for high pressure annealing were given in Ref. [15]. For comparative studies, the FePt:Ag thin films were also annealed without the use of the applied pressure in a vacuum furnace ($p < 10^{-3}$ Pa) (named as room pressure below). The microstructures of thin films were studied by employing an x-ray diffractometer (XRD) equipped with a thin film attachment using Cu $K\alpha$ radiation and a transmission electron microscope (TEM). The size of FePt grains and ordered domains was determined from bright-field and dark-filed TEM images in sample regions of ~25 μm^2, respectively, and the dark-filed images were made by using (001) and (110) $L1_0$-superlattice reflections. The size of $L1_0$ ordered domains was also determined from the broadening of superlattice diffraction peaks using the Williamson-Hall method [16]. The degree of $L1_0$ ordering S was calculated by [17]

$$S^2 = \frac{I_{(hkl)_{L1_0}}[(f_{Co}+f_{Pt})^2(P\varphi(\theta))]_{(111)}}{I_{(111)}[(f_{Co}-f_{Pt})^2(P\varphi(\theta))]_{(hkl)_{L1_0}}}$$

where $I_{(111)}$ and $I_{(hkl)_{L1_0}}$ are the integral intensities for the (111) diffraction peak of the $A1$+$L1_0$ phases and the (hkl) diffraction peak of the $L1_0$ phase, respectively; P is the multiplicity factor, $\varphi(\theta)$ is the angle factor, and f is the atomic scattering factor.

The volume fraction of Ag was calculated by the direct contrast method and the lattice parameter of the as-deposited FePt films was determined according to XRD patterns [18]. The coercivity of annealed FePt:Ag thin films was measured by employing a vibrating sample magnetometry with a magnetic filed of 21 kOe at room temperature.

3. Results and Discussion

XRD studies show that as-deposited thin films possess a disordered $A1$ structure of FePt phase [see the inset in Fig. 1(a)]. The grain size of the as-deposited films is about 5 nm similar to our previous studies [19]. No detection of Ag diffractions in the as-deposited thin films

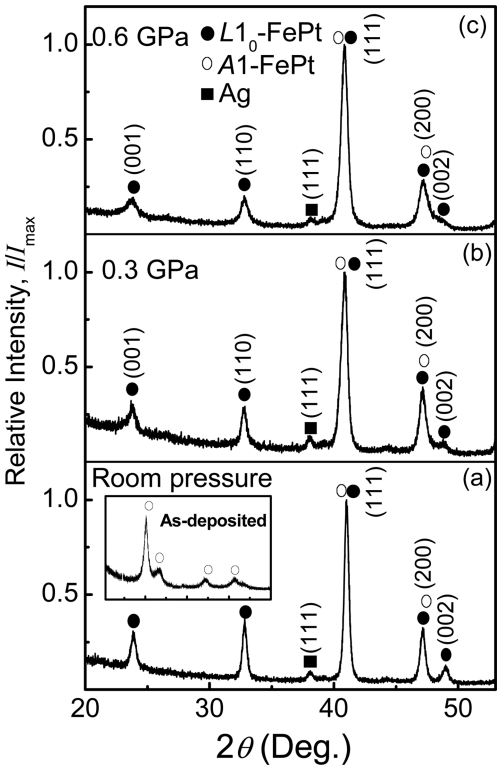

Fig. 1. XRD spectra of FePt:Ag nanocomposite thin films annealed at a temperature of $T = 873$ K for 30 min under various pressures up to 0.6 GPa. As-deposited thin films (see the inset) have a disordered face-centered-cubic (fcc) structure.

indicates Ag atoms existing in the FePt lattice, which can be further verified by the larger value of lattice parameter $a = 3.865$ Å for the FePt:Ag films than that $a = 3.846$ Å for pure FePt films (XRD pattern of pure FePt is not shown here), which may be due to the substitution of Fe atoms with a smaller atomic radius of 1.72 Å by Ag atoms with a larger atomic radius of 1.75 Å. After annealing at 873 K for 30 min under room pressure, the $L1_0$-superlattice (001) and (110) reflections appear, indicating the occurrence of $L1_0$ ordering transition of the FePt phase [see Fig. 1(a)]. The appearance of Ag (111) diffraction peak indicates that Ag is separated from the FePt lattice during the annealing process, yielding FePt:Ag nanocomposite thin films as reported by the previous works [20]. With the increase of annealing pressure to 0.6 GPa, the diffraction peaks are widened indicating the size of the $L1_0$ ordered domains is reduced by the high pressure (see Fig. 1). The relative intensity of Ag diffraction is almost invariable with the increase of applied pressure, demonstrating the separation of Ag independent of the applied pressures with a volume fraction of 10% determined from the XRD pattern. XRD calculations from the broadening of $L1_0$-superlattice reflections reveal that the

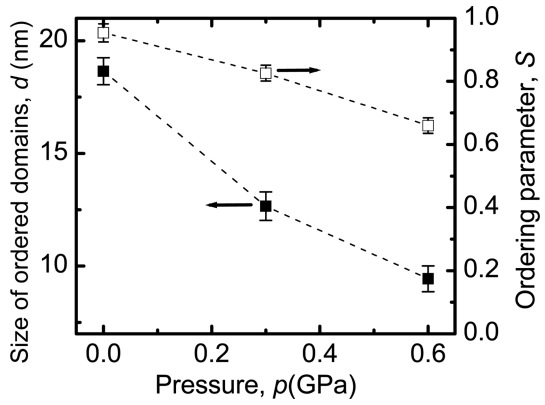

Fig. 2. Pressure dependence of $L1_0$ ordered domain size d (■) and ordering parameter S (□) of FePt:Ag nanocomposite thin films annealed at 873 K for 30 min. The size of $L1_0$ ordered domains decreases steeply with the increase of pressure, while the ordering parameter S shows a slight decrease with pressure.

size, $d \sim 9$ nm, of $L1_0$-FePt ordered domains for the films annealed under 0.6 GPa is much smaller than that $d \sim 19$ nm for those annealed under room pressure (see Fig. 2), which is in good agreement with that yielded from TEM observations [see Figs. 3(a) and (b)]. This demonstrates that annealing under a high pressure leads to an obvious reduction of $L1_0$-ordered domain size for $L1_0$-FePt: Ag

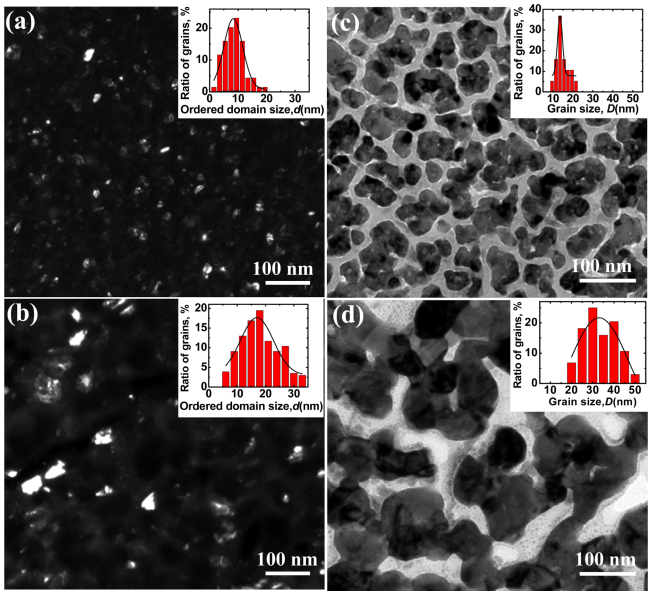

Fig. 3. (Color online) TEM dark-field (a, b) and bright-field (c, d) images as well as the grain and ordered domain size distributions (see the insets) of FePt:Ag nanocomposite thin films after 873 K annealing at (a, c) a high pressure of $P = 0.6$ GPa and (b, d) room pressure. The TEM dark-field images were made using the (001) and (110) $L1_0$-superlattice reflections.

nanocomposite thin films. The ordering parameter S shows a slight decrease from $S = 0.95$ to 0.65 as the pressure increases to 0.6 GPa, implying that the $L1_0$ ordering transition at 0.6 GPa dominantly depends on the nucleation of $L1_0$ ordered domains. A nucleation-promoted $L1_0$ ordering of FePt thin films has been reported in previous studies [21]. On the other hand, the size of $L1_0$-FePt grains in the nanocomposite film is also reduced by the high pressure annealing [see Figs. 3(c) and (d)]. The average grain size of $D = 13$ nm for the films annealed under 0.6 GPa is much smaller than that $D = 34$ nm for those annealed under room pressure.

From TEM images it can be obviously observed that the size of both the $L1_0$ ordered domains and FePt grains that are yielded at high pressure (0.6 GPa) has a narrow distribution. Most $L1_0$ domains locate in the range of 4-12 nm in the $L1_0$-FePt:Ag films prepared under 0.6 GPa, while those produced under room pressure in the range of 8-30 nm [see Figs. 3(a) and (b)]. A similar result is also obtained for grain size distribution [see Figs. 3(c) and (d)], where a smaller grain size of ~13 nm and a more uniform size distribution are yielded after high-pressure annealing. These studies demonstrate that $L1_0$-FePt:Ag nanocomposite thin films with small and uniform size for $L1_0$-FePt nanocrystals can be successfully prepared under high pressures.

The development of this unique microstructure in $L1_0$-FePt:Ag nanocomposite thin films can be understood by the pressure effects on nucleation and growth processes of $L1_0$ ordered domains as well as on the growth process of FePt grains. For $L1_0$ ordering phase transition of FePt crystals, taking the pressure into account and assuming that the interfacial energy γ is independent on the pressure P, the critical free energy ΔG^* required to form an $L1_0$ nucleus is given by [18]

$$\left(\frac{\partial(\Delta G^*)}{\partial P}\right)_T = -\frac{32\pi\gamma^3}{3}\frac{\Delta V}{\Delta G_V^3},$$

where the ΔG_V and ΔV are the Gibbs free energy and average volume differences between the $A1$ and $L1_0$ phases per unit volume in FePt system, respectively. The ΔG_V and ΔV are negative for the $L1_0$ ordering transition in FePt system, indicating that the ΔG^* decreases with the increase of pressure. This demonstrates that high pressure can enhance the nucleation rate of $L1_0$ ordered domains inside the FePt grains. Previous studies show that the growth of the $L1_0$ ordered domains and grains in FePt thin films depends on atomic diffusions [13, 19]. The high pressure constrains atomic diffusions during the $L1_0$ ordering and thus inhibits the growth of both the ordered

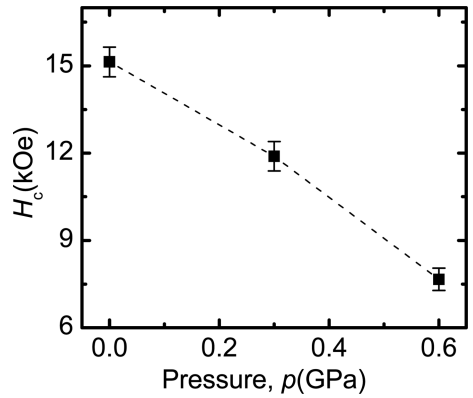

Fig. 4. Pressure dependence of the coercivity of FePt:Ag nanocomposite thin films annealed at a temperature of T = 873 K for 30 min.

domains and the grains. The high nucleation rate combined with the low growth rate yields the $L1_0$ ordered domains with a small and uniform size. This is similar to the previous reports by Zhang *et al.* which demonstrate that high pressures, just like deformation strains [22, 23] and temperatures [24], not only can modify the microstructures but also can induce the preferred orientation of the NdFeB/a-Fe nanocrystrals [25].

With increasing annealing pressure from room pressure to 0.6 GPa, the coercivity of $L1_0$-FePt:Ag nanocomposite thin films decreases from H_c = 15.1 to 7.6 kOe (see Fig. 4), which is attributed to the effect of high pressure on the ordering parameter S of FePt:Ag thin films (see Fig. 2). This provides an alternative route to tune the coercivity of $L1_0$-FePt:Ag magnetic recording media.

4. Conclusion

The present studies on FePt:Ag nanocomposite thin films demonstrate that, with increasing pressure from room pressure to 0.6 GPa at 873 K, the average size for both the $L1_0$ ordered domains and the grains of FePt phase can be reduced from d = 19 nm and D = 34 nm to d = 9 nm and D = 13 nm, respectively, and their size distributions are improved into a narrow range. This can be attributed to the promoted nucleation rate and inhibited growth rate of the $L1_0$ ordered domains in the FePt:Ag films under high pressures, and that the growth of FePt grains in the films are impeded at high pressure. The present study gives a direct clarify for the effects of the annealing pressure on the ordering process and the formed microstructure of the FePt:Ag particle films and opens the door for studying the character and physical mechanism of the atomic migration during the ordering process, which is of great importance for understanding the ordering process and reducing the ordering temperatures of FePt particle films.

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