Effect of Nd-Doping on the Microstructure and Magnetic Properties of $Nd_X(Fe_{47.5}Pd_{52.5})_{100\text{-}X}$ Films

Jianjun Huo, Gang Cheng, Yusong Du, Kuang Pan and Lin Li

Abstract In order to investigate the effect of rare earth Nd doping on FePd alloy thin films, the samples of $Nd_x(Fe_{47.5}Pd_{52.5})_{100\text{-}x}$ ($x = 0, 2, 2.7, 3.4, 4$) films were prepared by a DC magnetic sputtering method. The microstructure and magnetic properties were characterized by XRD, EDS, PPMS et al. The XRD data indicated that the addition of rare earth element Nd could significantly shorten the annealing time and the annealing temperature from the disordered FCC phase to the ordered FCT phase and increase the driving force of the phase transition. In addition, the appropriate addition of Nd element also has the role of grain refinement. The grain size could reach 29–14 nm and the appropriate grain size was conducive to the exchange coupling between the grains. The hysteresis loop of the films showed that the coercivity (Hc) and remanence ratio (Mr/Ms) first increased with the increase of Nd content sharply and then decreased. When the content of rare earth $x = 2.7$, the maximum coercivity was 3.05 kOe. The changes of coercivity and remanence ratio with the increase of annealing temperature also first increased and then decreased, and reached the maximum at 550 °C.

Keywords FePd films · Nd doping · Heat treatment · Magnetization

Introduction

With the rapid development of information technology, the demand for large capacity information storage devices is increasing rapidly. It has been paid attention to by the researchers in the past to search for high density magnetic recording

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devices. 1L_0 ordered phase FePd alloy (K_U = 10^7erg/cm^3) with high magnetocrystalline anisotropy and high coercivity. Theoretically, The maximum magnetic energy product is 48.0 MGOe [1]. These unique and excellent comprehensive properties are considered to be one of the best materials for ultrahigh density magnetic recording media and micro-electromechanical systems [2].

In recent years, a lot of research work mainly focused on the origin of the ordered $L1_0$ phase FePd alloy with high magnetocrystalline anisotropy [3–6] and to explore a variety of physical and chemical methods for the preparation of various alloy films, such as FePd alloy film [7–9], FePd/Fe multilayer film, [10] nanowire [11] and nano particles [12]. In order to improve the magnetic properties of the alloy (film), doping or alloying is the main method to improve the properties of materials [13–15]. The results show that if the FePd alloy nanocrystalline particles added in the C element, it will significantly hinder the diffusion of Fe and Pd atoms and it can inhibit the conversion of FePd nanoparticles from disordered FCC phase to ordered FCT phase [16], the comprehensive performance of the alloy can be improved.

At present, the effects of rare earth elements on the magnetic properties of FePd alloy thin films and their role in the microstructure evolution and order-disorder phase transition have not been systematically studied. In this paper, a series of Nd–Fe–Pd thin films were prepared by DC magnetic sputtering. The effects of Nd content and annealing temperature on the structure and magnetic properties of $Nd_x(Fe_{47.5}Pd_{52.5})_{100\text{-}x}$ thin films were studied by changing the content of rare earth Nd and annealing temperature.

Experiment

The thin film samples of $Nd_x(Fe_{47.5}Pd_{52.5})_{100\text{-}x}$ (x = 2, 2.7, 3.4, 4) were prepared by ultrahigh vacuum multi target magnetron sputtering. Rare earth Nd doped FePd layer by alternating deposition method. Nd rare earth films were uniformly placed on the FePd composite target (the purities of the ingredients were better than 99.9 wt%) and the content of rare earth in FePd layer was controlled by changing the number of rare earth films. It could be considered that the addition of rare earth will not change the proportion of the FePd layer and the total thickness because the rare earth was very few in the sputtering. In the experiment, the purity of the rare earth was not less than 99.5%. Before using, the Nd target was carefully cleaned and placed on the sputtering target of excitation. Before the deposition of thin films, the “pre sputtering” ready for 30 min to remove the oxide layer and the target surface impurities. In this study, $Nd_x(Fe_{47.5}Pd_{52.5})_{100\text{-}x}$ thin films were prepared by FJL560B4 ultra-high vacuum magnetron sputtering and the vacuum degree of the sputtering system was better than 6.5×10^{-5} Pa. The sputtering gas was argon and the sputtering pressure was 2.0 Pa. The films were sealed by argon filled under vacuum condition (10^{-1} Pa) and annealing in muffle furnace. Annealing temperature at 500, 550 and 600 °C, the holding time was 30 min. The deposition rates measured by an AMBIOS XP-2 stylus profilometer; the structure of annealed films was determined by Bruker D8-ADVANCE X ray diffractometer (XRD) using Co Kα radiation; the elemental composition analyzed by a JSM-5600LV scanning electron microscope equipped with EDS; magnetic properties of the samples were measured and analyzed by physical parameter testing system (PPMS-9T).

Results and Discussion

Figure 1 shows X-ray diffraction patterns for $Nd_x(Fe_{47.5}Pd_{52.5})_{100-x}$ (x = 0, 2, 2.7, 3.4, 4) thin film samples annealed at 550 °C for 30 min. As can be seen from the graph, the undoped film samples are basically composed of FCC phase at the same annealing conditions. When the content of Nd is 2 at.%, the weak FCT phase diffraction peak can be observed. With the further increase of Nd content, the intensity of the diffraction peak of FCT phase increases gradually. When the Nd content increases to 4 at.%, it is obvious to see the FCT phase diffraction peak, which is an ordered FCT phase, which means that the addition of Nd element can promote the phase transition of FCC—FCT. The result is that the phase transition temperature of FePd alloy films decreases with the increase of Nd content.

According to the diffraction data of alloy thin films, the lattice parameters of the FCC phase have been derived, and the results are shown in Table 1. Table 1 shows that the lattice parameter a increases in a near-linear fashion with increasing of Nd concentration. This indicates that the Nd atoms dissolved into the FCC phase, forming a solid solution, which leads to a cell-volume expansion resulting from the fact that the Nd atom radius is larger than those of both Fe and Pd atoms.

We calculated the c/a ratio and the order degree S^2, from the XRD data, and the results are displayed in Table 1 and Fig. 2. We can see that with the increase of Nd doping amount, the corresponding sample c/a ratio was decreased gradually; the order degree increased to a certain extent. This indicates that the addition of rare earth element Nd can enhance the driving force of phase transformation and

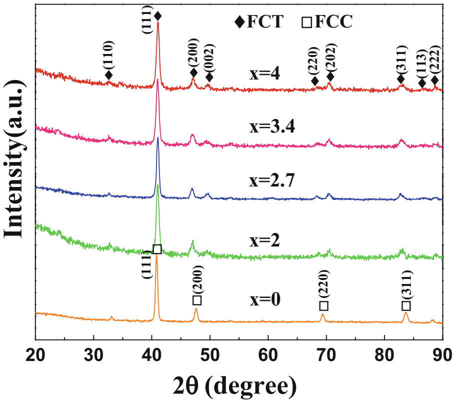


Fig. 1 XRD patterns of $Nd_x(Fe_{47.5}Pd_{52.5})_{100-x}$ films annealed at 550 °C for 30 min

Table 1 Lattice parameters of $Nd_x(Fe_{47.5}Pd_{52.5})_{100-x}$ films

Nd content *x* (at.%)	Lattice constant a = b (nm)	Lattice constant c (nm)	c/a
0	0.3854	0.3733	0.96860
2	0.3865	0.3739	0.96739
2.7	0.3872	0.3744	0.96694
3.4	0.3877	0.3748	0.96672
4	0.3882	0.3752	0.96651

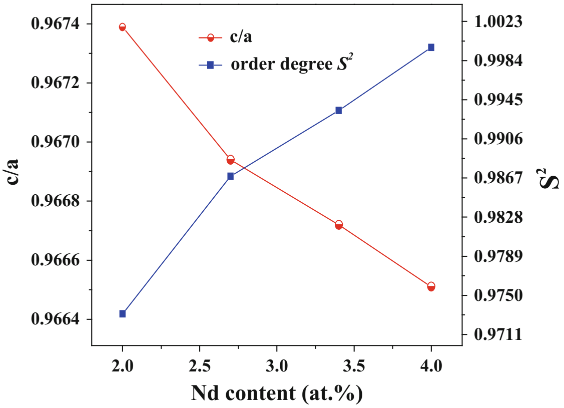


Fig. 2 Relationship of order degree and the ratios of c/a with the change of Nd content

contribute to the occurrence of phase transition in thin films. Figure 3 displays with the increase of Nd content, (002)/(200) peak intensity ratio increased gradually, it also shows that the control of the content of doping of rare earth Nd can adjust the ordered and disordered FePd phase ratio.

By using XRD data and Scherrer equation, we obtain the relationship between the grain size of the FCT phase and the content of rare earth, and the results are shown in Fig. 3. It can be seen from the figure that with the increase of the content of rare earth, the grain size is almost linearly reduced, Therefore, the rare earth element Nd has the role of grain refinement in the microstructure of the thin films. In the process of preparing samples, we can not only control the size of grain growth by changing the heat treatment conditions, but also can effectively control the size of the grains by adding rare earth elements.

Figure 4 shows the EDS data of the thin film samples, in which the samples were analyzed by surface scanning. The results showed that the films were composed of $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$.

The XRD results obtained for $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$ films annealed at various temperature for 30 min are shown in Fig. 5. Figure 5 shows that the as deposited films were disordered FCC structure, and the (002) reflection appears in the XRD patterns when the annealing temperature is no less than 500 °C. At this point the phase transformation from FCC to FCT phase is not completed, because the (200) reflection has not fully split into two reflections ((200) and (002)). When the

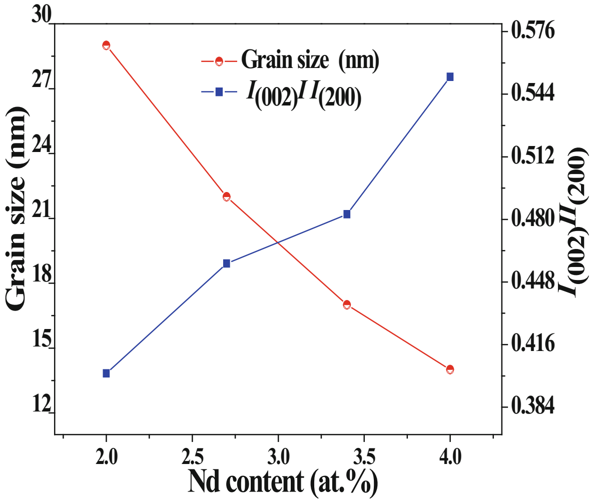


Fig. 3 Relationship of grain size and the ratios of I(002)/I(200) with the change of Nd content

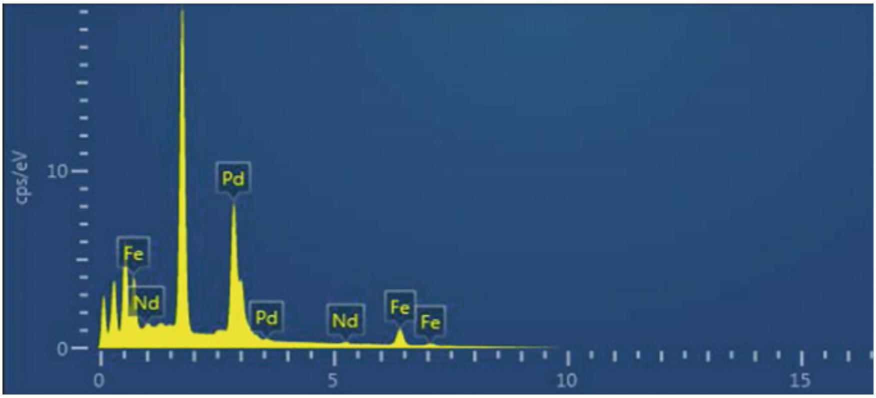


Fig. 4 EDS data of the $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$ film

annealing temperature is 550 °C, the (110), (200), (002), (220) and (202) reflection can be clearly observed. It shows that the structure of the films is mainly composed of FCT phase. After the addition of rare earth element Nd, the phase transition of FePd thin film is very sensitive to the annealing temperature and time, and the rare earth element Nd can effectively reduce the phase transition temperature or shorten the annealing time greatly. We could derive the values of the average grain sizes by means of Scherrer's formula, and we obtained the relationship between the grain size of $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$ thin film (x = 2.7) and annealing temperature. These values are included in Table 2. The grain size of FCT phase increases with the increase of annealing temperature.

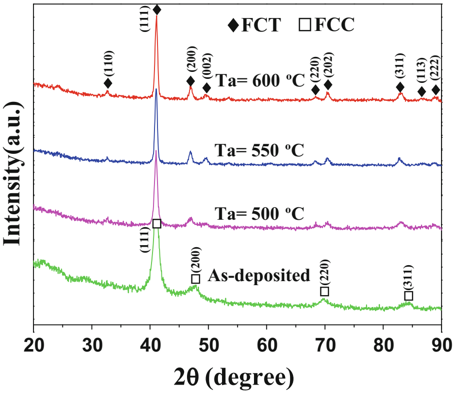


Fig. 5 XRD patterns of $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$ films annealed at different temperatures for 30 min

Table 2 Grain size at different annealing temperatures

Temperature (°C)	500	550	600
Grain size (nm)	19.8	22	28.2

Figure 6 illustrates the effect of Nd concentration on the magnetic properties of the $Nd_x(Fe_{47.5}Pd_{52.5})_{100\text{-}x}$ ($x = 0, 2, 2.7, 3.4, 4$) films. The obtained results are also included in Fig. 7. The inset in Fig. 6 shows that the Hc of the films first increase rapidly as the Nd content increases to $x = 2.7$, At the same time, the coercivity (Hc) of the film reaches the maximum, and then shows a more gradual decrease for x values from 2.7 to 3.4. Hc again decreases rapidly with further increasing of Nd content. As show in Fig. 7, we find that the relationship between remanence ratio (Mr/Ms) and the Nd content is similar to that between the coercivity (Hc) of the films and the Nd content.

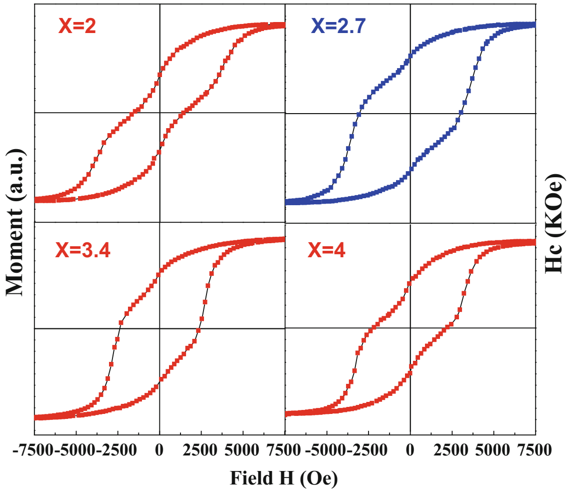
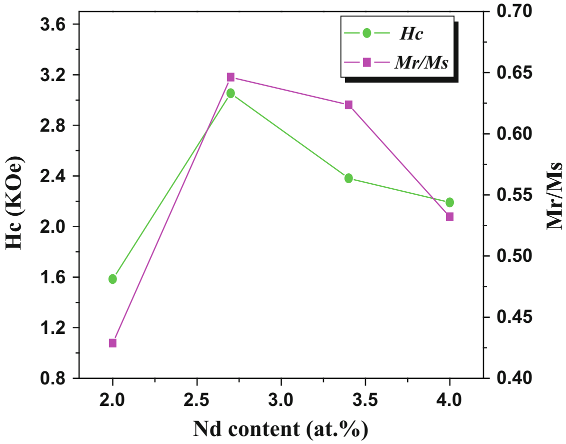


Fig. 6 Magnetic hysteresis loops of $Nd_x(Fe_{47.5}Pd_{52.5})_{100\text{-}x}$ films annealed at 550 °C for 30 min

Fig. 7 Hc, Mr/Ms versus Nd content



The factors that affect the coercivity are the magnetic anisotropy constant, the exchange coupling coefficient between grains, the concentration of FCT phase and the degree of order. According to the model of Kneller and Hawig [17], exchange coupling effect of the hard magnetic phase (k) and soft magnetic phase (m) is determined by the grain size. In the system of exchange coupled nanocomposite-magnet, the critical size of the exchange-coupling can be calculated according to the following formula:

$$b_{cm} = \pi(A_m/2K_k)^{1/2} \tag{1}$$

where A_m is the exchange interaction energy of soft magnetic phase, K_k is the magnetic anisotropy constant of the hard magnetic phase. In order to obtain a strong exchange coupling magnetic phase, the grain size of soft phase should be about equal to b_{cm}. The result shows that, when the grain size is less than 20 nm and uniform size, the exchange coupling effect between soft and hard magnetic phase can not only enhance the remanence Br, but also can increase the coercivity (Hc), so as to obtain high magnetic energy product. From the experimental data of XRD film, under the same heat treatment conditions, the more the concentration of rare earth Nd, the intensities of the FCT phase characteristic peaks (110), (200) (002) were stronger, and the splitting degrees of diffraction peak (200) and (002) were greater. This shows that the larger the volume fraction of FCT phase in the film, the higher the degree of order, the greater the anisotropy constant. When x exceeds 2.7, it is possible that the grain size is smaller than the optimum size of the exchange coupling, and lead to the coupling between soft and hard magnetic phase is weakened. Another possible reason is that the concentration of rare earth Nd exceeds the solid solution range of the FePd alloy, which makes the rare earth elements gather around the grain, which increases the distance between the grains and weakens the exchange coupling effect, which leads to further decreasing in Hc.

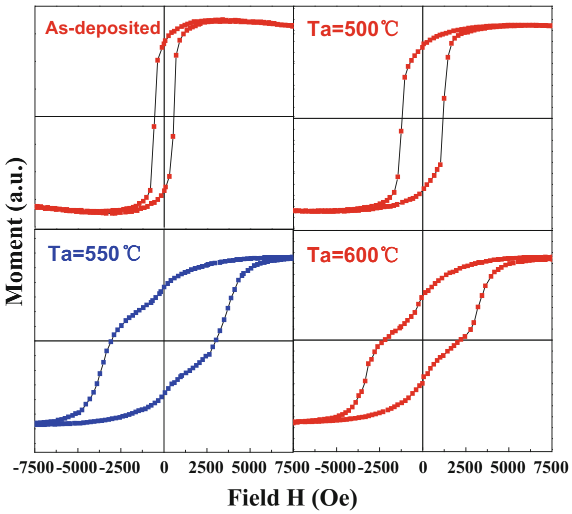


Fig. 8 Magnetic hysteresis loops of $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$ films annealed at different temperatures for 30 min

These factors added together, the maximum value of the coercivity and remanence ratio (Hc = 3.05 kOe, Mr/Ms = 0.646) appeared at x = 2.7.

Figure 8 shows the effect of annealing temperature on the magnetic properties of the $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$. The curve of the coercivity Hc and remanence ratio Mr/Ms with the change of annealing temperature were shown in Fig. 9. Peak values for both the coercivity Hc (Hc = 3.05 kOe) and the remanence ratio (Mr/Ms = 0.646) are reached at annealing temperature of 550 °C. The rise in Hc with annealing time is mainly due to the improvement in the chemical ordering of the FCT phase, leading to an increase in the anisotropy constant K_k. The relationship between the coercivity and the anisotropy constant can be expressed as follows:

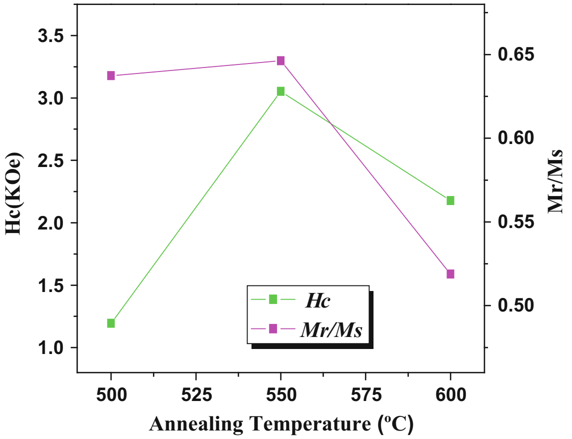


Fig. 9 Hc, Mr/Ms versus annealing temperature

$$Hc = K_k/\mu_0 M_{sm} \quad (2)$$

where M_{sm} is the saturation magnetization of the soft magnetic phase and K_k is the anisotropy constant of the hard magnetic phase. The higher remanence ratio suggests that exchange-coupling occurs between the soft magnetic phase and the hard magnetic phase. When the annealing temperature is higher than 550 °C, the coercivity and remanence ratio are beginning to decline. The reason is that when the annealing temperature increases, the grain size becomes larger, and the optimum size of coupling is removed, which leads to the decrease of coupling effect. Another possibility is because when the annealing temperature is too high, rare earth elements separate out from FePd alloys and enriched in grain boundaries, and the distance between the grains become larger, which affects the exchange coupling effect between grains, while the coercivity and remanence ratio also decreased. This is why coercivity and remanence ratio decreases with increasing of annealing temperature for FePd films.

Conclusion

The addition of rare earth element Nd in FePd alloy film can significantly shorten the transition time from FCC phase to FCT phase and decrease the annealing temperature, which indicates that adding moderate amount of rare earth Nd can increase the driving force of phase transformation. When small amounts of Nd are substituted for FePd, the Nd atoms dissolve into the FCC phase, forming a solid solution. The addition of Nd leads to an increase in the degree of ordering S and a decrease in the average grain size. The function relationship between the coercivity of FePd thin films and the rare earth Nd content increases sharply and then decreases. For $Nd_x(Fe_{47.5}Pd_{52.5})_{100\text{-}x}$ (x = 0, 2, 2.7, 3.4, 4) alloys films, the maximum value of the coercivity and remanence ratio (Hc = 3.05 kOe, Mr/Ms = 0.646) are obtained in x = 2.7. With the increase of annealing temperature, the change of $Nd_{2.7}(Fe_{47.5}Pd_{52.5})_{97.3}$ alloys films also first increases and then decreases, and the maximum value of Hc = 3.05 kOe has obtained at 550 °C for 30 min. Therefore, a small amount of rare earth doped (x < 2.7 at.%) and appropriate temperature conditions can improve the magnetic properties of the films.

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