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Effect of Post Annealing on the Microstructure and Magnetic Properties of NdFeB/α-Fe/NdFeB Thin Films*

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Abstract: A series of nanocomposite thin films, composed of $Nd_2Fe_{14}B$ and α-Fe, has been prepared by DC-magnetron sputtering combined ion beam sputtering onto Si (100) substrates. The effects of post annealing on the microstructure and magnetic properties of [NdFeB/α-Fe/NdFeB]-type thin films have been investigated. The X-ray diffraction (XRD) study showed that annealing of the films for 30 min at temperatures 550, 600, 650, 700 ℃ resulted in the appearance of diffraction peaks, characteristic for $Nd_2Fe_{14}B$ tetragonal structure, α-Fe and Nd_2O_3 phases. The investigation using the Vibrating Sample Magnetometer (VSM) with a maximum applied field of 2 T indicated that with the increase of the annealing temperature, the magnetic properties of the multilayer films were improved and reached peak value at 650 ℃ ($H_{ci} = 41.72$ kA·m^{-1}, $M_r/M_s = 0.4$, $(BH)_{max} = 30.35$ kJ·m^{-3}), after which the magnetic properties were decreased greatly. Along with the increase of the thickness of α-Fe layer from $T_{α\text{-}Fe} > 16$ nm, the coercivity H_{ci}, saturation magnetization M_s, and remanence ratio M_r/M_s all declined. As the Atomic Force Microscope (AFM) indicated, after being annealed at 650 ℃ for 30 min, the sample was showed fine surface morphology with grain size 60 nm ≤ $d_{α\text{-}Fe}$ ≤ 80 nm and 100 nm ≤ dNdFeB ≤ 150 nm.

Key words: $Nd_2Fe_{14}B$; multilayer films; sputtering; thermal annealing; magnetic properties
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Miniaturization of microelectromagnetic devices (MEMs) and magnetic recording media increases the demand for NdFeB permanent magnet thin films with high magnetic energy. In recent years, nano-composite exchange coupled magnets consisting of a fine mixture of hard- and soft-magnetic phases[1] have attracted much attention for the development of permanent magnets because a large maximum energy product [$(BH)_{max}$] in excess of 800 kJ·m^{-3} has been predicted according to micromagnetic calculations[2,3]. Such films have been prepared by magnetron sputtering[4~6], electropulsing heating amorphous alloys[7] and pulsed laser deposition[8]. At present, the permanent magnet properties of the nanocomposite films has remained some what low level, only in the range of 80 ~203 kJ·m^{-3}[9], although the energy density above 88% of the theoretical limit has been achieved in sintered NdFeB magnets. The discrepancy between the predicted and actual energy products is primarily attributed to the difficulty in obtaining the optimum microstructures that were employed for the theoretical models. It is well known that a number of technological parameters including sputter method, sputter gas pressure, annealing temperature (or deposition temperature), buffer layer materials and sample composition can affect the microstructure of NdFeB films and thus the hard magnetic properties[10~12]. Considering the high deposition rate of magnetron sputtering and the ability to obtain super thin film with ion beam sputtering, samples of nanocomposite film in this paper were prepared using both methods. Herein, we investigate the effect of annealing temperature on the structure, surface morphology and magnetic properties of sputtered NdFeB/α-Fe/NdFeB film.

1 Experimental

Samples were prepared by magnetron sputtering combined ion beam sputtering from a $Nd_2Fe_{14}B$ sintered target and a pure Fe target under a base pressure of better than 4.5×10^{-5} Pa. The sputtering conditions were as follows, the Ar working gas pressure of 1.5 Pa for $Nd_2Fe_{14}B$ and 2.5×10^{-2} Pa for Fe, incident power of DC-100 W for $Nd_2Fe_{14}B$ and 20 W for Fe. The distance between the $Nd_2Fe_{14}B$ target and

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Si (100) water-cooled substrate was 70 mm. The filament electric current was 7.5 A for Fe. The deposition rates under above conditions were 0.2062 nm $\cdot s^{-1}$ for $Nd_2Fe_{14}B$ and 0.0452 nm $\cdot s^{-1}$ for Fe, respectively. Then all the samples were post-annealed under argon at different temperatures for 30 min.

The X-ray diffraction (XRD) patterns of the samples were acquired on a Rigaku. D/Max2500 X-ray powder diffractometer. The products were observed using a KYKY2800 scanning electron microscope (SEM) and CSPM4000 atomic force microscope (AFM). The magnetic properties of the samples were measured on LDJ 9600 Vibrating Sample Magnetometer (VSM).

2 Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the films of NdFeB (200 nm)/α-Fe (16 nm)/NdFeB (200 nm) deposited at room temperature, and subsequently annealed at 550, 600, 650 and 700 ℃ for 30 min in an Ar atmosphere. After annealed, a $Nd_2Fe_{14}B$-type hard magnetic phase formed, accompanied by a trace of Nd_2O_3 and α-Fe. The $Nd_2Fe_{14}B$-type phase is randomly oriented in all annealed films. The diffraction peaks increase with increasing the annealing temperature. In addition, a Si (100) peak is clearly observed but not in all samples, because the thickness of the samples is not well proportioned after being deposited.

As shown in Fig. 2, selected area Scanning Electron Microscope (SEM) study confirms the amorphous structure of the as-deposited film. The subsequent annealing transformed the films into a stack of microcrystalline grains . Increasing the annealing temperature resulted in an increased number of larger sized grains of uniform shape. After annealed at 650 ℃ for 30 min, the sample shows the best microstructure. This is consistent with the XRD results.

Fig. 3 shows the AFM micrographs of samples annealed at 650 and 700 ℃ for 30 min respectively. The sample annealed at 650 ℃ shows a fine microstructure with the grain sizes for both α-Fe and the $Nd_2Fe_{14}B$ phases at 60 nm $\leq d_{\alpha\text{-Fe}} \leq$ 80 nm and 100 nm $\leq d_{NdFeB} \leq$ 150 nm. And the grain size became larger when annealing temperature increased to 700 ℃.

Shown in Fig. 4 is the hysteresis loops measured with VSM to a maximum field of 2 T in the direction parallel to the film plane. The hysteresis loops at room temperature show that the as-deposited amorphous film is magnetically soft and that the coercivity develops after annealing and forming the 2∶14∶1 structure.

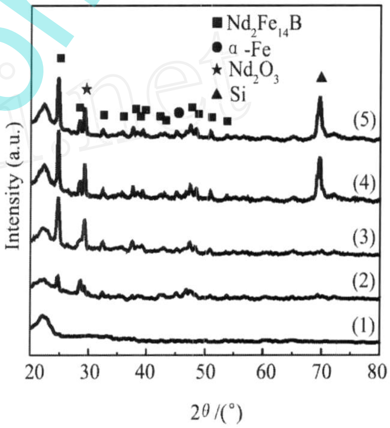

Fig. 1 XRD patterns of NdFeB (200 nm)/α - Fe (16 nm)/NdFeB (200 nm) films (1) as-deposited, (2) 550 ℃, (3) 600 ℃, (4) 650 ℃, (5) 700 ℃

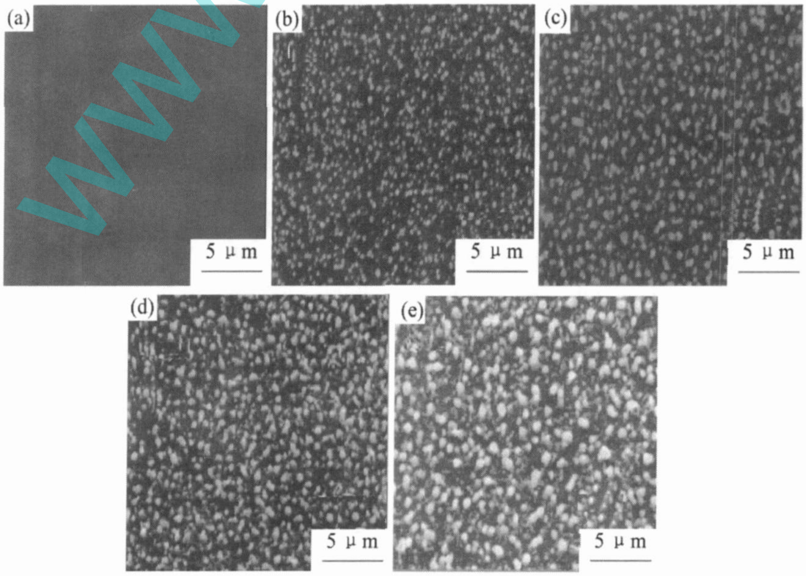

Fig. 2 SEM images of NdFeB (200 nm)/α-Fe (16 nm)/NdFeB (200 nm) samples (a) as-deposited, (b) 550 ℃, (c) 600 ℃, (d) 650 ℃, (e) 700 ℃

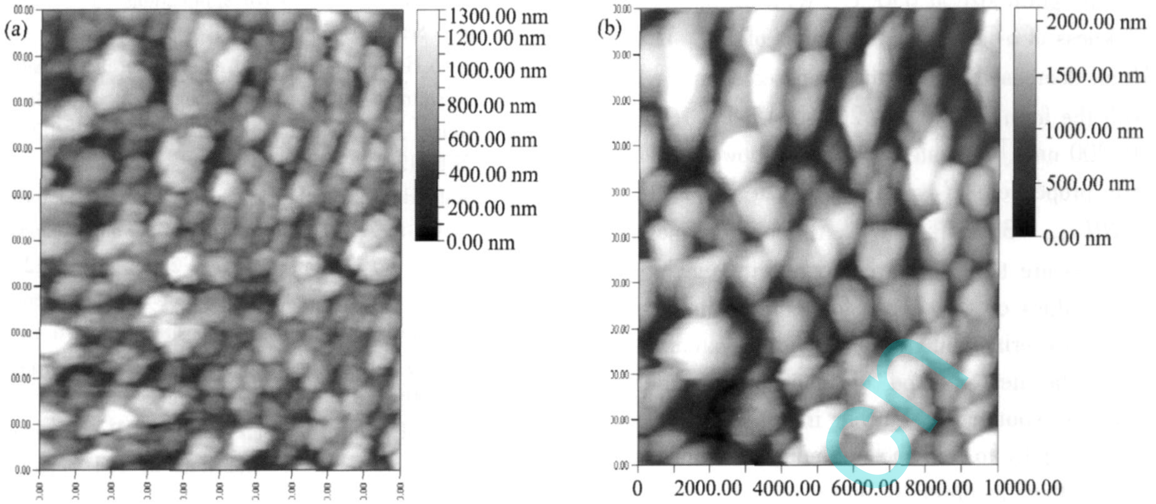

Fig. 3 AFM image of NdFeB (200 nm) /α-Fe (16 nm) /NdFeB (200 nm) annealed at different temperatures (a) 650 ℃ and (b) 700 ℃

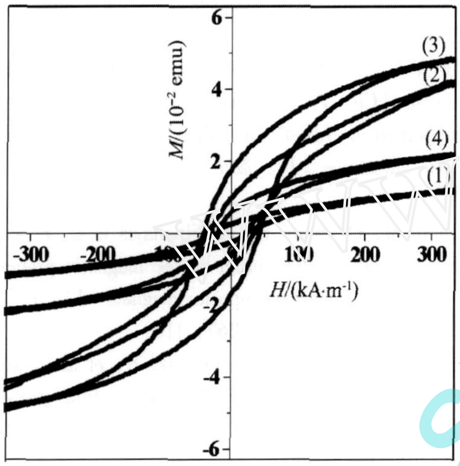

Fig. 4 Hysteresis loops of NdFeB (200 nm) /α-Fe (16 nm) /NdFeB (200 nm) films (a) 550 ℃, (b) 600 ℃, (c) 650 ℃, (d) 700 ℃

As can be seen in Table 1, the coercivity field H_{ci}, remanence M_r and saturation M_s increase with increasing the annealing temperature from 550 ℃ to 650 ℃, and all the values decrease after 650 ℃, which is in agreement with the XRD results.

In this paper, we have also prepared [NdFeB (200 nm) /α-Fe (26 nm) /NdFeB (200 nm)] and [NdFeB (200 nm) /α-Fe (39 nm) /NdFeB (200 nm)] films in order to compare with the former one. In Table 2, the coercive field H_{ci}, saturation magnetization M_s, and remanence ratio M_r/M_s are plated against the thickness of α-Fe. It is natural that H_{ci} decreases with increasing volume of α-Fe. There are two reasons. First, there is a decrease in the effective anisotropy constants $K_{eff} = f_s K_s + f_h K_h$, where f_s, f_h and K_s, K_h represent the volume fractions and anisotropy constants of the soft and hard components, respectively. Second, adding a soft phase tends to enhance the average size of the soft regions, which leads to a reduction of the nucleation field. However, M_s and M_r/M_s in larger α-Fe film is smaller than that in small α-Fe film. This may arise from the heterogeneous distribution of local demagnetizing fields owing to the distribution of shape and size of grains, which reduce the squareness of demagnetization curves.

Table 1 Magnetic properties of NdFeB (200 nm)/α-Fe (16 nm)/NdFeB (200 nm) films annealed at different temperatures

Annealing temperature/ ℃	H_{ci}/ (kA m^{-1})	M_r (emu)	M_s (emu)
550	18.29	0.004	0.012
600	24.34	0.009	0.042
650	41.72	0.019	0.048
700	31.96	0.011	0.041

Table 2 Magnetic characteristic of NdFeB/α-Fe/NdFeB films with different α-Fe thickness annealed at 650 ℃

Thickness of α-Fe/nm	H_{ci}/ (kA m^{-1})	M_s/ emu	M_r/M_s
16	41.72	0.048	0.396
26	32.74	0.039	0.318
39	23.55	0.022	0.282

3 Conclusion

A series of NdFeB/α-Fe/NdFeB nanocomposite films with different thicknesses of α-Fe layer has been prepared by DC magnetron sputtering combined ion beam sputtering. The crystallite of $Nd_2Fe_{14}B$ was confirmed to increase with the annealing temperature and showed fine grain size at 650 ℃. With an increase of the thickness of α-Fe layer, the values of H_{ci}, M_s and M_r/M_s all decreased. Of all the prepared samples, the film with the form of [NdFeB(200 nm)/α-Fe(16 nm)/NdFeB(200 nm)] annealed at 650 ℃ showed the best magnetic properties: $H_{ci} = 41.72$ kA·m^{-1}, $M_r/M_s = 0.4$, $(BH)_{max} = 30.35$ kJ·m^{-3}. Although the magnetic properties are too poor to compare with the ideally estimated values or with those for more realistic situations, the experimental results provide a valuable insight into the new method of magnetron sputtering combined ion sputtering. Further investigation is necessary, especially to find the optimum conditions with this new method in order to obtain proper grain size, which will then enhance H_{ci}, M_s and M_r/M_s, and hence $(BH)_{max}$.

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