Fabrication and Magnetic Properties of Exchange-Coupled Nd-Fe-B/Fe Nanocomposite Thin Films

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Thin films which consist of randomly distributed $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Fe phases were fabricated on glass substrates by rf sputtering. With increasing a number of Fe chips on Nd-Fe-B target from 0 to 6, the remanence B_r of the films increased from 6.4 to 15.6 kG, while the coercivity iH_c reduced from 2.1 to 0.34 kOe at room temperature after annealing at 873 K for 10 min. In the case of $\text{Nd}_{4.3}\text{Fe}_{88.4}\text{B}_{7.3}$ film, fabricated with 4 Fe chips, $B_r = 12$ kG and $iH_c = 1.3$ kOe were obtained and typical spring-back behavior was observed. Based on the temperature dependence of magnetization, volume fraction of α -Fe phase was estimated to be $V_{\text{Fe}} = 67\%$. These results indicate the exchange coupling between $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Fe phases. The iH_c value of the $V_{\text{Fe}} = 67\%$ film is larger than that of recently fabricated Nd-Fe-B/ α -Fe multilayer films with $V_{\text{Fe}} = 40 \sim 50\%$.

Key words : nanocomposite magnet, $\text{Nd}_2\text{Fe}_{14}\text{B}$, thin films, spring-back, micromagnetic calculation

1. Introduction

Exchange-coupled nanocomposite magnets were predicted theoretically to show remarkably high maximum energy product¹⁾. They were fabricated mainly by rapid quenching, but the maximum energy product was much lower than those expected theoretically. The primary reason is thought to be a difference between actual and ideal nanostructures. It is difficult to optimize the structure and crystallite alignment precisely in rapid quenching process, while, in thin films, they can be controlled by changing thickness of films and substrate temperature. Highly oriented $\text{Nd}_2\text{Fe}_{14}\text{B}$ thin films were fabricated^{2,3)} by sputtering with heated substrates. We succeeded in fabricating exchange-coupled Nd-Fe-B/Fe multilayers⁴⁾, and obtained the coupling strength between hard and soft layers by comparing the micromagnetic calculation with the experiments⁵⁾. Exchange coupling between hard and soft layers and remanence enhancement have also been reported in Nd-Fe-B/Fe/Nd-Fe-B trilayers⁶⁾. However coercive field values in these films are still smaller than those expected.

One of the authors recently made a micromagnetic calculation⁷⁾, which have shown that a random arrangement geometry of soft and hard phases gives higher coercivity than that of the multilayer geometry. Thus it is expected that the random arrangement nanocomposite film show better magnetic properties.

In this study, we report the magnetic properties of thin films which consist of randomly distributed $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Fe phases and compare the results with those of multilayers⁴⁾.

2. Experimental Procedures

Thin films were fabricated on glass substrates by rf magnetron sputtering. The base pressure of the sputtering system was below 7.5×10^{-7} Torr and the Ar pressure during sputtering was 5.0×10^{-3} Torr. The films have a form of Ti (100 nm)/Nd-Fe-B ($d_{\text{Nd-Fe-B}}$ nm)/Ti (100 nm) with $d_{\text{Nd-Fe-B}}$ varied from 100 to 2000 nm. The composition of films were adjusted by putting different numbers of Fe chips (314 mm²) on the $\text{Nd}_{13}\text{Fe}_{70}\text{B}_{17}$ target ($\phi = 76$ mm). Since as-sputtered Nd-Fe-B films were confirmed to be amorphous, all of the films were annealed at 873 K for 10 min to crystallize the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The composition of as-sputtered Nd-Fe-B films were determined by electron probe micro analysis (EPMA), which is given in Table 1.

3. Results and Discussion

We have performed a micromagnetic calculation of the magnetization curves using Landau-Lifshitz-Gilbert equation, which is similar to the previous report⁵⁾. Figure 1 shows the results of calculated coercivity as a function of the volume fraction of α -Fe, with the geometry of multilayer type $[\text{Nd-Fe-B/Fe}]_N$ and of a random distribution type. The same values of parameters as those in Ref. 5 were used, that is, intergrain or interlayer coupling constants J_H (between cells of $\text{Nd}_2\text{Fe}_{14}\text{B}$) and J_S (between cells of Fe) are 2.0×10^{-2} J/m² and exchange constants J_{HS} (between cells of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Fe) is $0.07 \times J_H$, crystal grain size is 15 nm, and the thickness of Nd-Fe-B layer is 30 nm in multilayer. At least for $V_{\text{Fe}} \geq 10\%$, iH_c in the random distribution geometry is higher than that in the multilayer case. A primary reason for the difference of iH_c in two arrangements will be the larger interfacial area between soft and hard cells in the random arrangement, which tends to prevent the soft cell moments, with the help of exchange coupling J_{HS} , from rotating toward the demagnetization field direction.

Figure 2 shows the film thickness dependence of iH_c and $4\pi I$ at the external field $H = 15$ kOe. As shown in Fig. 2(a), iH_c of $\text{Nd}_{9.2}\text{Fe}_{77.4}\text{B}_{13.4}$ and $\text{Nd}_{4.3}\text{Fe}_{88.4}\text{B}_{7.3}$ films exhibits a maximum at $d_{\text{Nd-Fe-B}} = 500$ nm, while that of $\text{Nd}_{2.0}\text{Fe}_{93.4}\text{B}_{4.6}$ film monotonically decreases with increasing $d_{\text{Nd-Fe-B}}$. Figure 2(b) shows that $4\pi I$ reduces sig-

Table 1 Chemical composition obtained from EPMA, volume fraction of α -Fe, V_{Fe} , coercivity, iH_c and remanence, B_r of the fabricated films with different number of Fe chips.

Number of Fe chips	Composition	V_{Fe} (%)	iH_c (kOe)	B_r (kG)
0	$\text{Nd}_{9.2}\text{Fe}_{77.4}\text{B}_{13.4}$	0 (+5)	2.1	6.4
4	$\text{Nd}_{4.3}\text{Fe}_{88.4}\text{B}_{7.3}$	67 (± 4)	1.3	12.0
6	$\text{Nd}_{2.0}\text{Fe}_{93.4}\text{B}_{4.6}$	76 (± 4)	0.34	15.6

Fig. 1 Calculated and observed coercivity values at room temperature, for random arrangements (■, □) and multilayer geometries (▲, △), plotted against α -Fe fraction, V_{Fe} .

nificantly for $d_{Nd-Fe-B} \leq 300$ nm, while it is roughly constant for $d_{Nd-Fe-B} \geq 500$ nm. The reason for the rapid decrease in magnetization for $d_{Nd-Fe-B} \leq 300$ nm would be a diffusion of Ti into the Nd-Fe-B layer by annealing, which could crystallize a non magnetic phase. When $d_{Nd-Fe-B}$ is large enough, the diffusion of Ti have little influence on magnetic properties.

Next we show the X-ray diffraction patterns for the films with $d_{Nd-Fe-B} = 500$ nm in Fig. 3. In the $Nd_{9.2}Fe_{77.4}B_{13.4}$ film, diffraction peaks of isotropic $Nd_2Fe_{14}B$ phase was observed in addition to the underlayer and overlayer Ti and Ti-oxide peaks. In the case of $Nd_{4.3}Fe_{88.4}B_{7.3}$ and $Nd_{2.0}Fe_{93.4}B_{4.6}$ films, α -Fe peaks appeared as expected, while no detectable trace of $Nd_2Fe_{14}B$ peaks was observed.

Figure 4 shows the temperature dependence of magnetization for the films with $d_{Nd-Fe-B} = 500$ nm, measured after applying and removing the field at 5 K. We performed this measurement to estimate the volume fraction of $Nd_2Fe_{14}B$ and α -Fe phases. Magnetization of $Nd_{9.2}Fe_{77.4}B_{13.4}$ film decreases with increasing temperature and almost vanishes at Curie temperature ($T_c = 585$ K) of $Nd_2Fe_{14}B$ phase. Although anomalous decrease of magnetization at $T_c(Nd_2Fe_{14}B)$ has also been observed in $Nd_{4.3}Fe_{88.4}B_{7.3}$ and $Nd_{2.0}Fe_{93.4}B_{4.6}$ films, magnetization values are still large for $T > T_c$. By combining this result with the X-ray experiments (Fig. 3), we may conclude that α -Fe coexists with that of $Nd_2Fe_{14}B$. Based on the shapes of magnetization curves, we have roughly estimated the volume fractions of $Nd_2Fe_{14}B$ and α -Fe phases, which are given also in Table 1. It should be noted that another anomaly is observed around 135 K, which could be ascribed to the spin orientation transition in the $Nd_2Fe_{14}B$ phase⁸⁾.

Magnetization curves for the films with $d_{Nd-Fe-B} = 500$ nm measured at room temperature are shown in Fig. 5. Magnetization at $H = 15$ kOe, $4\pi I_{15}$ appears to be almost saturated. With increasing V_{Fe} , $4\pi I_{15}$ increases, while iH_c decreases. The ratios of remanence B_r to $4\pi I_{15}$ are 0.81 and 0.88, respectively, for $V_{Fe} = 67\%$ and 76% films. These values are larger than the calculated $B_r/4\pi I_s$ of 0.76 and 0.78, respectively, assuming that $Nd_2Fe_{14}B$ and α -Fe grains with random orientations are not exchange coupled.

Results of X-ray and Magnetization measurements have, thus, shown the existence of both hard ($Nd_2Fe_{14}B$) and

Fig. 2 (a) Coercivity iH_c , and (b) Magnetization, $4\pi I$ at $H = 15$ kOe, as a function of Nd-Fe-B thickness $d_{Nd-Fe-B}$.

Fig. 3 X-ray diffraction patterns for (a) $Nd_{9.2}Fe_{77.4}B_{13.4}$, (b) $Nd_{4.3}Fe_{88.4}B_{7.3}$ and (c) $Nd_{2.0}Fe_{93.4}B_{4.6}$ films.

soft (α -Fe) phases in $Nd_{4.3}Fe_{88.4}B_{7.3}$ and $Nd_{2.0}Fe_{93.4}B_{4.6}$ films. In order to investigate the exchange coupling between the two phases, we measured the minor loops of demagnetization curves at room temperature, which is shown in Fig. 6. In the $Nd_{4.3}Fe_{88.4}B_{7.3}$ film, typical spring-back behavior was observed, in which 75 % of B_r value was recovered when the field was reduced to zero from iH_c . This behavior is in contrast to the case of $Nd_{9.2}Fe_{77.4}B_{13.4}$ film,

Fig. 4 Temperature dependence of magnetization for (a) $\text{Nd}_{9.2}\text{Fe}_{77.4}\text{B}_{13.4}$, (b) $\text{Nd}_{4.3}\text{Fe}_{88.4}\text{B}_{7.3}$ and (c) $\text{Nd}_{2.0}\text{Fe}_{93.4}\text{B}_{4.6}$ films.

Fig. 5 Magnetization curves of (a) $\text{Nd}_{9.2}\text{Fe}_{77.4}\text{B}_{13.4}$, (b) $\text{Nd}_{4.3}\text{Fe}_{88.4}\text{B}_{7.3}$ and (c) $\text{Nd}_{2.0}\text{Fe}_{93.4}\text{B}_{4.6}$ films at room temperature.

where the recovered magnetization at $H = 0$ is considerably small. The values of coercive field in the present films are plotted in Fig. 1, in comparison with iH_c in multilayer films, and corresponding calculations. Data points of the present random geometry films for $V_{\text{Fe}} \geq 67\%$ appear to connect smoothly with the corresponding calculation line. The iH_c value of the $V_{\text{Fe}} = 67\%$ film is larger than that of multilayer films with $V_{\text{Fe}} = 40 \sim 50\%$. If we assume that iH_c of the two types of films show a monotonic depen-

Fig. 6 Demagnetization curves of (a) $\text{Nd}_{9.2}\text{Fe}_{77.4}\text{B}_{13.4}$ and (b) $\text{Nd}_{4.3}\text{Fe}_{88.4}\text{B}_{7.3}$ films, showing minor loops.

dence on V_{Fe} for $V_{\text{Fe}} = 40 \sim 70\%$, these results seem to be in agreement with the micromagnetic calculations. It is clear that preparing films with smaller V_{Fe} is necessary in order to compare with the calculation in more detail.

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