Fabrication of Exchange-Coupled α-Fe/Nd-Fe-B Multilayer Thin-Film Magnets

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Abstract— Multilayers having the form of Ti/Fe/[Nd-Fe-B/Fe]x5/Ti/glass were fabricated on glass substrates by means of rf sputtering and subsequent annealing. We have confirmed that these films keep clear multilayer structure and Nd2Fe14B grains were randomly aligned. We have observed the spring-back behavior in the magnetization curves, which confirms the exchange coupling between Fe and Nd-Fe-B layers. Moreover, micromagnetic calculations applied for nanocomposite magnets have been performed, which indicated that good alignment of hard magnetic phase and crystal grain size less than 10 nm are extremely important factors to derive the potential for nanocomposite magnets.

I. INTRODUCTION

Nanocomposite magnets[1] are expected to have a potential for high performance magnetic powders for bonded magnets. The magnetic properties of nanocomposite magnets strongly depend on their nanostructures, so it is necessary to investigate the relation between magnetic properties and structures in detail. Nanocomposite magnets are obtained mainly by melt-spinning or rapid-quenching process[2], [3]. However, it is not easy to control the nanostructure by using such a method. As proposed by Skomsk and Coey[4], a multilayered two phase magnet, consisting of alternating hard and soft magnetic layers has the advantage that individual layer thickness can be controlled precisely. Al-Omari and Sellmyer[5] found the exchange-coupled behavior in CoSm/FeCo bilayer films, while a remanence-enhancement behavior have been reported by Parhofer et al.[6] observed for Nd-Fe-B/Fe/Nd-Fe-B trilayers. We have succeeded in fabricating exchange-coupled α-Fe/Nd-Fe-B multilayer films with Ti both for underlayers and overlayers, and reported the dependence of magnetic properties on layer thickness[7]. Moreover, we have estimated the coupling strength between α-Fe and Nd-Fe-B layers to be about 10% of the FelFe and Nd-Fe-B/Nd-Fe-B couplings by comparing the experiments with micromagnetic calculations[8]. In this paper, we will report the more advanced experimental and calculated results and discuss the directions of improvement for magnetic properties of nanocomposite magnets.

II. EXPERIMENTAL PROCEDURES

Thin films of Nd-Fe-B single layer and α-Fe/Nd-Fe-B multilayer were fabricated by rf magnetron sputtering system with 99.9 % Fe metal and Nd13Fe50B17 alloy targets. The base pressure of the sputtering system was below 4.0x10⁻⁴ Pa and the Ar pressure during sputtering was 8.0x10⁻¹ Pa. The multilayers have the form of Ti/Fe/(Nd-Fe-B/Fe)x5/Ti/glass, with the thickness of two Ti layers dTi = 30 nm, Fe layers varied over the range of dFe = 0 - 50 nm, and Nd-Fe-B layers dNd-Fe-B = 0 - 100 nm. All the films were annealed at 873 or 923 K for 30 minutes with the pressure below 4.0x10⁻⁴ Pa to crystallize the Nd2Fe14B phase. The magnetization curves were measured at room temperature by means of vibrating sample magnetometer with a maximum field of 1.2 MA/m applied parallel to the film plane. X-ray diffractometer was used to study the structural properties of the films. The composition of the as-sputtered Nd-Fe-B films were determined by the EPMA. Transmission electron microscopy (TEM) images and Auger profiles were used to confirm the multilayer structure of annealed samples.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

According to the EPMA results, the composition of the as-sputtered Nd-Fe-B films were found to be Nd13.1Fe50B17, so the each Nd-Fe-B layer in α-Fe/Nd-Fe-B multilayer films is expected to be almost single phase containing Nd2Fe14B grains. We have confirmed that Ti(30 nm) both for underlayers and overlayers can keep the films unoxidized upon annealing[7]. Figure 1 shows the x-ray diffraction profile for multilayer with dNd-Fe-B = 30 nm and dFe = 10 nm. The peaks of randomly aligned Nd2Fe14B phase and α-Fe phase can be observed. Figure 2 shows TEM images for multilayers with dNd-Fe-B = 30 nm and (a)dFe = 5 nm, (b)dFe = 30 nm. We can confirm that Fe and Nd-Fe-B layers keep clear multilayer structure upon annealing. Figures 3(a) and (b) show demagnetization curves and minor loops for the films of dFe = 5 nm and dFe = 30 nm with fixed dNd-Fe-B = 30 nm,
Fig. 1. X-ray diffraction profile for Ti(30 nm)/Fe(10 nm)/Nd-Fe-B(30 nm)/Fe(10 nm) × 5/Ti(30 nm)/glass multilayer.

Fig. 2. TEM images of Ti(30 nm)/Fe(dFe)/Nd-Fe-B(30 nm)/Fe(dFe) × 5/Ti(30 nm)/glass multilayers: (a) dFe = 5 nm, (b) dFe = 30 nm.

Fig. 3. Demagnetization curves with minor loops for Ti(30 nm)/Fe(dFe)/Nd-Fe-B(30 nm)/Fe(dFe) × 5/Ti(30 nm)/glass multilayers: (a) dFe = 5 nm, (b) dFe = 30 nm.

respectively[7],[8]. The spring-back behavior is clearly seen, which strongly suggests that α-Fe and Nd2Fe14B phases are exchange coupled.

We have measured the magnetization curves of various multilayer films with different dFe and dNd-Fe-B systematically. Figure 4 shows the coercivity $H_c$ and remanence $B_r$ as a function of $d_{Fe}$ and $d_{Nd-Fe-B}$ for Ti(30 nm)/Fe(dFe)/Nd-Fe-B(30 nm)/Fe(dFe) × 5/Ti(30 nm)/glass samples. Figures 4(a) and (b) show the $d_{Fe}$ dependence with fixed $d_{Nd-Fe-B}$ and $d_{Nd-Fe-B}$ = 30 nm, respectively. Figure 4(c) shows the $d_{Nd-Fe-B}$ dependence with fixed $d_{Fe}$ = 10 nm, and Fig.4(d) shows the $d$ dependence when $d = d_{Nd-Fe-B} = d_{Fe}$. As shown in Figs.4(a) and (b), $H_c$ decreases with increasing $d_{Fe}$, while $B_r$ increases monotonously with increasing $d_{Fe}$ except for $d_{Fe}$ = 30 nm. In the case of Fig. 4(c), $B_r$ gradually goes down with increasing $d_{Nd-Fe-B}$ except for the case of $d_{Nd-Fe-B} < 30$ nm and $T_a = 923$ K. $H_c$ is roughly constant for $d_{Nd-Fe-B} > 20$ nm, while, after taking a small maximum around $d_{Nd-Fe-B} = 15$ nm, it decreases drastically for
Fig. 4. Dependence of $B_r$ and $H_{cj}$ on the layer thickness $d$ in Fe/Nd-Fe-B multilayers annealed at 873K and 923K. (a) as a function of $d_{Fe}$ with fixed $d_{Nd-Fe-B} = 10$ nm, (b) as a function of $d_{Fe}$ with fixed $d_{Nd-Fe-B} = 30$ nm, (c) as a function of $d_{Nd-Fe-B}$ with fixed $d_{Fe} = 10$ nm, and (d) as a function of $d = d_{Fe} = d_{Nd-Fe-B}$. Solid lines are guides to the eye.

$d_{Nd-Fe-B} < 10$ nm. In Fig. 4(d), we can see that $H_{cj}$ exhibits a maximum when the layer thickness $d$ is around 10-15 nm. $B_r$ slightly increases with decreasing $d$ for $d > 20$ nm, after taking a small maximum around $d = 10-20$ nm, it decreases for thinner layer thickness. For all cases in Fig. 4, the difference of $B_r$ and $H_{cj}$ between the case of Ta = 873 K and Ta = 923 K are significant for small $d_{Nd-Fe-B}$. However, any obvious structural difference could not be observed from the TEM images and Auger profiles. More precise investigation will be needed to explain this phenomena.

We found that calculated $H_{cj}$ shows a maximum for $d_{Nd-Fe-B} = d_{cry}$ (the crystal grain size of Nd$_2$Fe$_{14}$B and Fe phase), so the peaks of $H_{cj}$ around $d_{Nd-Fe-B} = 15$ nm in Figs. 4(c) and (d) indicate that $d_{cry} = 15$ nm in our system[8]. In the case of $d_{Nd-Fe-B} > d_{cry} = 15$ nm, a number of Nd$_2$Fe$_{14}$B grains between Fe layers decreases with decreasing $d_{Nd-Fe-B}$. When $d_{Nd-Fe-B} = d_{cry} = 15$ nm, there is only one Nd$_2$Fe$_{14}$B grain between Fe layers. Then, if the coupling strength between Fe and Nd-Fe-B phase is relatively small, the Nd$_2$Fe$_{14}$B grain approaches to be magnetically isolated grain, so $H_{cj}$ increases with decreasing $d_{Nd-Fe-B}$ around $d_{Nd-Fe-B} = d_{cry} = 15$ nm. In the case of $d_{Nd-Fe-B} < 15$ nm, the Nd$_2$Fe$_{14}$B grain can not grow larger than at least $d_{Nd-Fe-B}$ for the direction of Fe layers, so the mean crystal grain size of Nd$_2$Fe$_{14}$B phase is considered to decrease with decreasing $d_{Nd-Fe-B}$. Then, $H_{cj}$ decreases with decreasing $d_{Nd-Fe-B}$ for $d_{Nd-Fe-B} < 15$ nm, whose mechanism will be discussed in section IV. Moreover, in the case of Fig. 4(c), the volume fraction of Fe phase increases with decreasing $d_{Nd-Fe-B}$, which is thought to be also the reason for the decrease in $H_{cj}$ for $d_{Nd-Fe-B} < 15$ nm.

We have found that, for all the $\alpha$-Fe/Nd-Fe-B multilayer films, the $d_{Fe}$ and $d_{Nd-Fe-B}$ dependence of magnetization is roughly in accordance with the estimation based upon the simple superposition of magnetization of the $\alpha$-Fe and Nd-Fe-B phases.

**IV MICROMAGNETIC CALCULATION FOR NANOCOMPOSITE MAGNETS**

We have performed a micromagnetic calculation compared with experiments for multilayers to estimate the coupling strength between Fe and Nd-Fe-B phase[8]. In this paper, we will report a micromagnetic calculation for nanocomposite magnets randomly distributed soft and hard phases. As shown in Fig. 5, the mesh model of the calculation is formed with $10 \times 10 \times 10$ cubic cells which correspond to crystal grains. The soft and hard magnetic grains are randomly distributed. A periodic boundary condition for three dimensional directions has been adapted to form mesh model without surface boundary. We consider a magnetocrystalline anisotropy energy and Zeeman energy for each cell in which only one magnetization exists. The magnitude of anisotropy
Fig. 5. Model of the micromagnetic calculations. A cell corresponds to a crystal grain. The exchange constant $J_{H}$ (between cells of Nd-Fe-B) and $J_{S}$ (of Fe) were fixed at $2.0 \times 10^{-2}$ J/m$^2$, while $J_{HS}$ (between Fe and Nd-Fe-B cells) was adjusted to be $2.0 \times 10^{-3}$ J/m$^2$ so as to best reproduce the experimental data for multilayers.

constant for Nd-Fe-B was taken to be $4.5 \times 10^6$ J/m$^3$ and that for Fe was neglected. Moreover, three kinds of exchange interactions between the cells has been used, in which two intralayer coupling constants $J_{H}$ (between cells of Nd-Fe-B) and $J_{S}$ (of Fe) are fixed to be $2.0 \times 10^{-2}$ J/m$^2$, which is comparable to the value adopted by Fukunaga et al[9]. The exchange constant $J_{HS}$ (between Fe and Nd-Fe-B cells) have been adjusted to be $2.0 \times 10^{-3}$ J/m$^2$ so as to best reproduce the experimental data for multilayers[8].

By solving Landau-Lifshitz-Gilbert equation for all cells, we have calculated the distribution of magnetization for all system in order to obtain J-H curves with d cry varied from 0 to 50 nm. Figures 6(a) and (b) show the calculated $H_{cJ}$ and $(BH)_{max}$ as a function of crystal grain size, respectively. The volume fraction of the Fe phase was fixed to be 50 %. As shown in Fig.6(a), the alignment of Nd-Fe-B phase is defined with the parameter $\eta$ which represents the distribution of magnetic easy direction for Nd-Fe-B phase. The parameter $1-\eta$ increases with increasing the rate of alignment of Nd-Fe-B phase. In both cases of $1-\eta = 0$ (isotropic) and 0.75 (anisotropic), $H_{cJ}$ increases with decreasing $d_{cry}$ for $d_{cry} > 10$ nm, because small $d_{cry}$ prevents the magnetization of Fe phase from reversing. The difference of magnetic properties between isotropic and anisotropic nanocomposite magnets arises drastically when $d_{cry} < 10$ nm. In the case that the Nd-Fe-B phases are randomly aligned, $H_{cJ}$ and $(BH)_{max}$ decrease with decreasing $d_{cry}$ when $d_{cry} < 10$ nm. With decreasing $d_{cry}$, effective coupling strength increases significantly, so that the magnetization of each grain comes to be oriented toward a certain direction against the magneto crystalline anisotropy in each grain. Then, the magnetocrystalline anisotropy in each grain is canceled out for the total magnetization in the system, so $H_{cJ}$ goes down. As a result, $H_{cJ}$ and $(BH)_{max}$ take a maximum around $d_{cry} = 10$ nm, which is considered to be the best size of crystal grain for isotropic nanocomposite magnets. Then, $(BH)_{max}$ is expected to be about 0.22 MJ/m$^3$. The mechanism of decrease in $H_{cJ}$ for $d_{cry} < 10$ nm is considered to be similar to that for multilayers in the case of Figs.4(c) and (d). On the other hand, in the case of oriented system, $H_{cJ}$ and $(BH)_{max}$ increases monotonously with decreasing $d_{cry}$. In this case, the direction of the total magnetization in the system is nearly the same as the magnetic easy direction of each grain, so that only the effect that small $d_{cry}$ prevent the magnetization reversal in Fe phase is reinforced without the cancellation of magnetocrystalline anisotropy in the case of isotropic magnets. Thus, $H_{cJ}$ keeps increasing with decreasing $d_{cry}$ for $d_{cry} < 10$ nm. Moreover, it should be noted that $(BH)_{max}$ is expected to be about 0.62 MJ/m$^3$ for $d_{cry} = 5$ nm. Namely, even if the coupling strength is about 10 % of
Fe/Fe or Nd-Fe-B/Nd-Fe-B coupling, $(BH)_{max}$ is expected to exceed that of Nd$_2$Fe$_{14}$B single phase magnets. We have confirmed that the good alignment of hard magnetic phase and the crystal grain size less than 10 nm are extremely important factors to derive a potential for nanocomposite magnets sufficiently.

V. CONCLUSIONS

We have fabricated exchange-coupled Fe/Nd-Fe-B multilayers by rf sputtering and obtained the magnetic properties as a function of layer thickness. Micromagnetic calculation applied for nanocomposite magnets indicated that the good alignment of hard magnetic phase and the crystal grain size less than 10 nm are extremely important factors to derive a potential for nanocomposite magnets sufficiently.

REFERENCES