Influences of Oxidation State of Nd-Rich Phase on the Coercivity of Nd-Fe-B/Nd Thin Films

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The Nd-rich phase of Nd-Fe-B sintered magnets, which contains some amount of oxygen, plays an important role for generating coercivity. However, the influence of interfacial microstructure between NdFe14B and Nd-rich phases has not been clear. In this study, NdFe14B/Nd(−O) interface was prepared by thin film technique and the influence of oxidation state of Nd-rich phase on the coercivity was investigated. A Nd-Fe-B layer was deposited by ultra high vacuum (UHV) magnetron sputtering, and the film was oxidized under low vacuum condition (low oxidation state) or Ar atmosphere (high oxidation state). A Nd layer was deposited on the oxidized Nd-Fe-B layer, and the film was annealed at 250–650 °C for 60 min. The coercivity of films oxidized in low oxidation state was recovered by annealing at 250–650 °C, and an amorphous phase was observed at the interface between NdFe14B and hcp Nd3O5 (+fcc NdO3) phases in the film annealed at 350 °C. On the other hand, the coercivity of films oxidized in high oxidation state was lower than that of films oxidized in low oxidation state, and it decreased more about 20% by annealing at 250–350 °C. However, an amorphous phase was not observed at the interface of these films. After annealing above 550 °C, the coercivity of films oxidized in both low and high oxidation state recovered drastically to the almost same value of as-deposited film. From the SAD patterns of TEM observation, a metastable C-Nd3O5 phase was present in the Nd-rich phase of these films. In addition, it is known that the wettability of Nd-rich phase improves at temperatures around 550 °C. Therefore, it is considered that the increase of coercivity is related to the improvement of fluidity of Nd-rich phase or the existence of C-Nd3O5 phase.

Keywords: neodymium-iron-boron thin films, neodymium-oxide, coercivity, interfacial microstructure

1. Introduction

As Nd-Fe-B sintered magnets show the highest energy products among permanent magnets, they are used in various applications. In these days, the usage of Nd-Fe-B sintered magnets for motors of hybrid electric vehicle (HEV) has grown, and Dy or Tb has been added for improving thermal stability of Nd-Fe-B sintered magnets. However, these rare-earth elements are expensive and their addition decreases stability of Nd-Fe-B sintered magnets. Therefore, these researchers have observed the interfacial microstructure. Vial et al.3) reported that the optimum annealing after sintering developed the smooth interface between NdFe14B and Nd-rich phases, and the coercivity grew about 150% of as-sintered sample. Sagawa et al.2) reported the Nd-rich phase have an fcc structure, and Ramesh et al.7) showed the Nd-rich phase contains oxygen about 20–50 at%. Makita and Yamashita5) detected that the Nd-rich phase forms an fcc NdO with two preferential orientation relationship between the NdFe14B and Nd-rich phases. Fukagawa and Hiroswa5) reported that an fcc NdO phase exists on the NdFe14B grains, and the fcc NdO phase is necessary for generating coercivity. According to Shinba et al.,6) the Nd-rich phase contains oxygen and the microstructure changes from crystallite to amorphous with decreasing the thickness of Nd-rich phase. Mo et al.7) reported that the crystalline structure of Nd-rich phase changes by amount of oxygen content. In our previous paper,8) we prepared NdFe14B/Nd-rich interface by using thin film technique and investigated the influences of oxidation on the coercivity and interfacial microstructure. We also reported the existence of an amorphous phase at the interface between NdFe14B and hcp Nd3O5 (+fcc NdO3) phases in the samples, which showed the recovery of coercivity by annealing.

However, the oxidation condition in our previous paper was constant, in which the Nd-Fe-B layers were oxidized in vacuum of 10−2–10−5 Pa, and the relationship between oxidation state and coercivity is still unclear. Therefore, in this study, the NdFe14B/Nd(−O) interface was fabricated by sputtering with a condition different from that in our previous paper, and the influence of oxidation state on coercivity was investigated by comparing the results with those in our previous work.

2. Experimental Procedure

The series of samples prepared in this investigation are summarized in Table 1. All films were prepared by ultra high vacuum (UHV) magnetron sputtering with base pressure of 1 × 10−7 Pa. A Nd-Fe-B layer with the thickness of 100 nm was deposited on Ta buffered MgO (001) substrate, which was heated at 680 °C (Hereafter, this as-deposited film is referred as “sample A”). The composition of target used for the preparation of Nd-Fe-B layer was Nd18Fe66B16. After deposition of Nd-Fe-B layer, films were cooled to room temperature and moved to another chamber. The films were...
kept for 120 min under low vacuum condition or Ar gas atmosphere to be oxidized. Oxidation in low vacuum (10^{-2}~10^{-5} \text{ Pa}) or in Ar gas atmosphere, is referred as “low oxidation state” or “high oxidation state”, respectively. The film oxidized in low oxidation state was named as “sample B(L)Nd” and the film oxidized in high oxidation state was named as “sample B(H)Nd”. The estimated oxygen content in these two oxidation states are shown in Table 2. After oxidation, the films were moved back to the UHV chamber and a Nd layer with the thickness of 2 nm was deposited on these oxidized Nd-Fe-B layers. Then, these films were annealed at 250–650°C for 60 min in the UHV chamber with vacuum of 10^{-7} \text{ Pa} (sample C(L)Nd (low oxidation state) and sample C(H)Nd (high oxidation state)). In addition, following four samples named as “sample B(L), B(H), C(L) and C(H)” were prepared in order to investigate the effects of Nd layer. Namely, Nd-Fe-B films were oxidized (sample B(L)Nd (low oxidation state) and sample B(H)Nd (high oxidation state)) and annealed at 250–650°C for 60 min (sample C(L)Nd (low oxidation state) and sample C(H)Nd (high oxidation state)) without Nd layer deposition. Finally, a Ta layer was deposited on the top of all films for the suppression of oxidation from air.

Magnetic properties were measured by a vibrating sample magnetometer (VSM) along the direction perpendicular to the film plane after applying a pulsed magnetic field of 6360 kAm^{-1}. Microstructure was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3. Results and Discussion

The remanences of samples with good squareness were around 0.72~0.80 T. The coercivities of samples were shown as standardized values. The coercivities of samples B(L)Nd-C(H)Nd were compared to that of sample A, and these values were evaluated by the ratio of coercivity ($RH_{cJ}$), which was defined by the following formula.

$$RH_{cJ} = \frac{H_{cJ}}{H_{cJ} (\text{as} - \text{depo.})} \times 100$$

Table 3 shows the $RH_{cJ}$ of samples B(L)Nd, B(H)Nd, B(L)Nd, and B(H)Nd. The samples B(L)Nd and B(L)Nd were oxidized in low oxidation state and the values of $RH_{cJ}$ were reported in our previous work. They show the $RH_{cJ}$ of 65~68%, which suggests that their coercivities decrease about 32~35% from the values of as-deposited samples by oxidation. On the contrary, $RH_{cJ}$ of samples B(H)Nd and B(H)Nd, which were oxidized in high oxidation state, are 35~38% and the samples show remarkable decrease in coercivity about 60%. From Table 3, this difference of $RH_{cJ}$ means that Nd-Fe-B layer was more oxidized in Ar gas than in low vacuum condition.

Figure 1 shows the annealing temperature dependence of ratio of coercivity measured for samples C(L)Nd, C(H)Nd, C(L), and C(H). The data obtained for sample A, B(L)Nd, B(H)Nd, B(L)Nd, and B(H)Nd are also shown.
annealing at 250–350°C. After annealing above 550°C, the $R_{H_J}$ recovers drastically to the same value of sample A, as shown in Fig. 1. These results suggest that there are two kinds of recovery in coercivity by annealing, which depends on the oxidation state of films. The first one occurs only for the samples oxidized in low oxidation state and annealed at low temperatures around 350°C. The second one occurs for samples oxidized in both low and high oxidation state after annealing at high temperatures above 550°C.

Figure 2 shows the XRD patterns of films with (a) low oxidation state and (b) high oxidation state. The films are (i) sample A, (ii) sample B$_{(L)}$Nd, sample C$_{(L)}$Nd which were annealed at (iii) 350, (iv) 550 and (v) 650°C, (vi) sample B$_{(H)}$Nd, and sample C$_{(H)}$Nd, which were annealed at (vii) 350, (viii) 550 and (ix) 650°C, respectively.

Figure 3 shows the high-resolution transmission electron microscopy (HRTEM) images of sample C$_{(L)}$Nd and C$_{(H)}$Nd, which were annealed at 350°C. In sample C$_{(L)}$Nd, which shows the $R_{H_J}$ of 100% and the recovery of coercivity by annealing, the authors reported that an amorphous phase exists at the interface between Nd$_2$Fe$_{14}$B and hcp Nd$_2$O$_3$ (+ fcc NdO$_x$) phases as shown in Fig. 3(a). However, in sample C$_{(H)}$Nd, which shows the $R_{H_J}$ of ~20%, such amorphous phase is not observed at the interface, and Nd$_2$Fe$_{14}$B and fcc NdO$_x$ phases contact directly, as shown in Fig. 3(b). These results mean that the amorphous phase plays an important role for removing the influences of oxidation and for the recovery of the coercivity. In addition, the oxidation state of Nd-rich phase is considered as an important factor for forming the amorphous phase. The amorphous phase cannot form during annealing in the samples oxidized in high oxidation state, in which large amount of hcp Nd$_2$O$_3$ phase is present. The authors suggested that the amorphous phase forms during the phase transformation from fcc NdO$_x$ to hcp Nd$_2$O$_3$ by annealing and releases strain between Nd$_2$Fe$_{14}$B and hcp Nd$_2$O$_3$ (+ fcc NdO$_x$) phases. It is known that the fcc NdO$_x$ is a metastable phase and the stability of hcp Nd$_2$O$_3$ is higher than that of fcc NdO$_x$. Therefore, in the samples oxidized in high oxidation state, it is considered that the hcp Nd$_2$O$_3$ is present and the amorphous phase does not form, which leads to no recovery of coercivity despite the sample after annealing at 350°C.
Figure 4 shows the HRTEM images of sample C (H) (Fig. 4(a)), which was oxidized in high oxidation state and then annealed at 550°C, and the selected area diffraction (SAD) patterns taken from the Nd-rich phase in the sample (Fig. 4(b)–4(e)). The HRTEM image shown in Fig. 4(a) reveals that Nd$_2$Fe$_{14}$B and Nd-rich phases contact directly. From the SAD pattern shown in Fig. 4(b), which was taken along $\frac{1}{2}000/C_{2211}/C_{2211}/C_{138}$ zone axis of Nd-rich phase, the Nd-rich phase in sample C (H) is found to be hcp Nd$_2$O$_3$ phase (Fig. 4(c)). In Fig. 4(b), there are some weak spots between (000) and (100) spots of the hcp Nd$_2$O$_3$ phase, which are attributed to the Nd$_2$Fe$_{14}$B phase close to the Nd$_2$O$_3$ phase.

The SAD patterns shown in Fig. 4(d), which was taken from another point of Nd-rich phase, reveals that fcc NdO$_x$ phase remains in sample C (H). Furthermore, weak super-lattice spots with space group $Ia_3$ are observed in the SAD pattern (Fig. 4(e)). The Nd oxide phase which belongs to the space group is only C-Nd$_2$O$_3$ and the phase has a cubic structure with lattice parameter of $a = 1.107$ nm. Researchers have observed this phase in Nd-Fe-B sintered magnets with high coercivity. Therefore, the appearance of C-Nd$_2$O$_3$ has possibility for leading the increase in coercivity of Nd-Fe-B films annealed at temperature above 550°C.

Another possibility of coercivity growth by annealing above 550°C is the cleaning effect of Nd-rich phase. Nishio et al. investigated the wettability of Nd-rich phase and measured a contact angle between Nd$_2$Fe$_{14}$B and Nd-rich phases during heat treatment. They reported that the contact angle changed and the fluidity of Nd-rich phase increased at the temperatures around 580°C. As the samples in this study were prepared by thin film technique, the oxygen content of Nd-rich phase in the samples of this study was lower than that in their specimen. Therefore, the temperature, at which the fluidity of Nd-rich phase improves and cleaning effect of Nd-rich phase to the surface of Nd$_2$Fe$_{14}$B occurs, can be considered to be lower temperature, and the coercivity increases at temperatures around 550°C. Furthermore, the annealing at high temperature seems to promote the crystallization of the hcp Nd$_2$O$_3$ phase, as shown in XRD pattern in Fig. 2(b).

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