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Research Report

Effect of Nano-sized Grain Boundary on Coercivity of NdFeB Magnets

Takashi Sato, Tetsu Ohsuna, Yuji Kaneko, Yukiko Takahashi, Kazuhiro Hono and Toshiyuki Shima

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ABSTRACT | The effects of the nano-grains and the grain boundaries in Nd-Fe-B magnets on the coercivity ($H_c$) were investigated through an analysis of the relation between the structure and magnetic properties of ternary Nd-Fe-B thin films. Nd-Fe-B films ranging from 2 to 50 nm in thickness (t) were grown aligned in the (001) direction of the Nd$_2$Fe$_{14}$B phase under all conditions. Atomic force microscopy (AFM) revealed that the morphology of the Nd-Fe-B film changed from islands to a continuous thin film with increasing t, based on the Volmer-Webber growth mechanism. This change indicates that magnetic state of the film shifts from single-domain particles to multiple-domain particles with increasing t. The maximum $H_c$ in as-prepared Nd-Fe-B thin films showed 19.5 kOe at t = 8 nm. From the initial magnetization curve and the AFM image, the film with t = 8 nm was composed of both single-domain particles and multiple-domain particles. In contrast, $H_c$ of Nd-Fe-B/Nd$_{36}$Cu$_{64}$ films post-annealed at 400°C was 26.1 kOe. The increase in $H_c$ results from the suppression of the exchange coupling between Nd$_2$Fe$_{14}$B grains separated by the grain boundary, which is enriched by non-magnetic elements of Nd and Cu.

KEYWORDS | Coercivity, Nd-Fe-B, Nano-structure, Grain Boundary, Nd-Cu, Thin Film, Sputter, Diffusion, Perpendicular Anisotropy

1. Introduction

Nd-Fe-B magnets(1) are widely used in various applications as a magnetomotive force because these magnets have a large maximum energy product ((BH)$_{max}$ ~60 kOe) and a high saturation magnetization ($M_s$ = 1.6 T)(2). In particular, a high coercivity of Nd-Fe-B magnets is required in high-temperature environments, such as motors in hybrid vehicles and electric vehicles. However, the coercivity of Nd-Fe-B magnet has been reported to be ~13 kOe only 20% of the theoretical value(3) estimated by both the magnetocrystalline anisotropy and the saturation magnetization. The coercivity was improved by using (Nd, Dy)-Fe-B alloys partially substituting Dy for Nd because the anisotropy field of the alloys is higher than that of Nd$_2$Fe$_{14}$B alloy.(4,5)

The reduction of Dy has been intensively investigated in order to solve the resource problem involving rare earth elements. Dy-diffusion processes in grain boundaries between the Nd-Fe-B grains have attracted much attention.(6-9) On the other hand, studies on the improvement of coercivity without Dy have also focused on the grain boundary.(10-14) For instance, W. F. Li et al. reported that an improvement in coercivity for sintered Nd-Fe-B magnets, including Cu, resulted from the formation of a Cu-rich grain boundary, indicating the suppression of the exchange coupling between neighbor Nd-Fe-B grains. The grain boundary is believed to be a key factor in improving the coercivity. Therefore, a number of studies using a thin film fabrication technique have been conducted in order to control both the microstructure and the boundary of Nd-Fe-B magnets.(15-24)

In the present study, in order to clarify the effect of the nano-grains and the grain boundaries of Nd-Fe-B magnets on the coercivity, ternary Nd-Fe-B thin films were formed by the direct-current (dc) magnetron sputtering method and their structure and magnetic properties were investigated. In particular, post-annealed Nd-Fe-B/Nd-Cu thin films have been successfully fabricated in order to elucidate the above effect.

2. Experimental

Cr/Mo/Nd-Fe-B/Cr thin films and Cr/Mo/Nd-Fe-B/Nd-Cu/Cr multilayered thin films were fabricated on
single-crystal MgO (100) substrates using a UHV-compatible dc magnetron sputtering system with a base pressure of less than $1 \times 10^{-8}$ Pa. The Ar gas pressure was maintained at 0.13 Pa during deposition. A 1-nm-thick Cr seed layer and a 20-nm-thick Mo buffer layer were epitaxially grown on MgO substrates at room temperature (RT). The substrate temperature was maintained at 625°C during the deposition of the Nd-Fe-B layer. A 10-nm-thick Cr layer was formed as a topmost layer at RT in order to prevent oxidation. Nd$_2$Fe$_{14}$B was formed by co-sputtering with Fe, Fe$_{80}$B$_{20}$, and Nd. Hereinafter, the numerical subscript of alloys denotes atomic percent (at%). The composition of the Nd-Fe-B layer was adjusted to Nd$_{15.2}$Fe$_{70.2}$B$_{14.6}$, which was a Nd-rich and B-rich composition compared to that of stoichiometric Nd$_2$Fe$_{14}$B. The thickness ($t$) of the Nd-Fe-B film ranged from 2 to 50 nm. Here, $t$ was estimated from the deposition rate of 0.04 nm/s and the deposition time.$^{(25,26)}$ The diffusion of Nd and Cu into the Nd-Fe-B layer was conducted by co-sputtering with both Nd and Cu onto the Nd-Fe-B layer at RT and subsequent annealing at 400 or 500°C for 1 h. Here, thickness of the Nd-Cu layer was 0.5 or 1 nm.$^{(26)}$

The composition of the films was determined by electron probe x-ray micro-analysis (EPMA). The structural analysis was performed by X-ray diffraction (XRD) with Cu K$\alpha$ radiation. The surface morphology was observed by atomic force microscopy (AFM) and the microstructure was analyzed by both high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). Energy dispersive X-ray spectroscopy (EDS) revealed the elemental distribution in the film. The magnetization curves were measured with a superconducting quantum interference device (SQUID) magnetometer in the field up to 70 kOe at RT. The magnetic field was applied in the perpendicular direction to the film and in the in-plane direction to confirm the magnetic anisotropy.

3. Results and Discussion

3.1 Effect of Morphology of Nd-Fe-B on Coercivity$^{(25)}$

Figure 1 shows XRD patterns for Nd-Fe-B films with $t = 2$ to 50 nm. The sharp diffraction peaks denoted by the asterisks are due to the MgO (100) substrate, and the peak from the Mo (200) is also observed clearly at around $2\theta = 58.6°$ for all of the films. The peak observed at $2\theta = 65.2°$ is identified as the diffraction from Fe (200) for the film with $t = 2$ nm. Moreover, the peaks from Nd$_2$Fe$_{14}$B (004) and (0010) appeared primarily at 29.3° and 78.3° for all of the films. However, for the films with $t = 20$ and 50 nm, the peaks from Nd$_{15.2}$Fe$_{70.2}$B$_{14.6}$ (200) and Nd (004) began to appear at 25.0° and 30.3°, respectively. The orientation of the film was also confirmed from a cross-sectional TEM image of the film with $t = 5$ nm, as shown in Fig. 2. The $c$ plane of the tetragonal Nd$_2$Fe$_{14}$B phase was clearly observed parallel to the film plane. These results indicate that the Nd$_2$Fe$_{14}$B phase grows with the (001) orientation.

Fig. 1 X-ray diffraction patterns for the Nd-Fe-B films with (a) $t = 2$ nm, (b) 5 nm, (c) 8 nm, (d) 10 nm, (e) 20 nm, and (f) 50 nm. Asterisks denote the peaks from the MgO (100) single-crystal substrate.

Fig. 2 Cross-sectional TEM image of the Nd-Fe-B film with $t = 5$ nm.
Figure 3 shows AFM images of the films with different \( t \). The surface morphology changed with \( t \) via the Volmer-Webber growth mechanism. Isolated islands, ranging from 20 to 100 nm, appeared and grew for \( t = 5 \) to 20 nm. Then, a continuous structure was formed for \( t > 20 \) nm.

The magnetization curves for various \( t \) are shown in Fig. 4. The magnetic easy axis is perpendicular to the film plane and corresponds to the direction of \( c \) axis, as shown in Fig. 1. The initial magnetization curves changed with increasing \( t \). In the cases of \( t = 2 \) and 5 nm, the initial magnetization curves show a slow start to magnetize and so could not be fully saturated below 20 kOe as an external magnetic field. In contrast, the initial magnetization curves of \( t = 8, 10, \) and 20 nm show a steep increase in each initial magnetization curve. The magnetization of the film with \( t = 50 \) nm increases steeply and saturates at approximately 10 kOe. The slow increase of the initial magnetization curve with increasing magnetic field indicates the rotation of magnetization by the single-domain particles. On the other hand, the steep increase in magnetization at a low magnetic field is dominated by the domain wall displacement in the multiple-domain particles.\(^{(27)}\) The change in the magnetic domain structure indicated by the initial magnetization curves corresponds to the growth of the particles, as shown in the AFM images (Fig. 3). The effect of \( t \) for the Nd-Fe-B thin films on the coercivity (\( H_{cJ} \)) is shown in Fig. 5. With decreasing \( t \), \( H_{cJ} \) increased in the films with \( t > 8 \) nm due to the change from the multiple-domain particles to the single-domain particles. In contrast, \( H_{cJ} \) in the films with \( t < 8 \) nm decreased remarkably with decreasing \( t \). This may be attributed to the distortion of the Nd\(_2\)Fe\(_{14}\)B structure. Here, \( H_{cJ} \) of the film showed a maximum value of 19.5 kOe at \( t = 8 \) nm, and the domain structure of the film consisted of a mixture of single-domain and multiple-domain particles.

![Figure 3](image3.png)

**Fig. 3** Atomic force microscopy images of the Nd-Fe-B films with various film thicknesses ((a) \( t = 2 \) nm, (b) 5 nm, (c) 8 nm, (d) 10 nm, (e) 20 nm, and (f) 50 nm).

![Figure 4](image4.png)

**Fig. 4** Magnetization curves for the Nd-Fe-B films with various film thicknesses ((a) \( t = 2 \) nm, (b) 5 nm, (c) 8 nm, (d) 10 nm, (e) 20 nm, and (f) 50 nm; solid lines: \( H \perp \) film plane, dashed lines: \( H \parallel \) film plane).

![Figure 5](image5.png)

**Fig. 5** Coercivity of the Nd-Fe-B thin film as a function of film thickness \( t \).
3.2 Effect of Grain Boundary on Coercivity

The magnetization curves of Nd-Fe-B (30 nm)/Nd-Cu (1 nm) thin films with different Cu concentrations x in the Nd$_{100-x}$Cu$_x$ layer are shown in Fig. 6, where x = 0, 18, 64, 78, and 100. These films were post-annealed at 500 °C for 1 h. As a reference, an Nd-Fe-B film without post-annealing was prepared, and the curves are shown in Fig. 6(f). The magnetic field of 45 kOe was not sufficient to saturate the magnetization in the in-plane direction, indicating the existence of a large perpendicular magnetic anisotropy. Here, $H_{cj}$ of 12.8 kOe was obtained for the film without post-annealing, and a steep increase in the initial magnetization curve below 7 kOe was observed. In contrast, a remarkable increase in $H_{cj}$ for the annealed specimen was observed, while the initial magnetization curve is similar. However, a large magnetic field was needed in order to saturate the magnetization. Here, $H_{cj}$ of the annealed film with the Nd layer (x = 0) increased slightly compared to that of the as-prepared Nd-Fe-B film. With increasing x in the Nd$_{100-x}$Cu$_x$ layer, $H_{cj}$ increased and exhibited a large value of 23 kOe at x = 64. $H_{cj}$ was drastically improved at Nd$_{36}$Cu$_{64}$ (at.%), even though the composition is far from that of the Nd-Cu eutectic alloy (Nd$_{70}$Cu$_{30}$). This may be associated with the effect of ternary or more complex compositions for the decrease in the solidification temperature. Eventually, the simultaneous diffusion of Nd and Cu elements into the Nd-Fe-B layer is effective in improving $H_{cj}$.

The effect of post-annealing on $H_{cj}$ for Nd-Fe-B and Nd-Fe-B/Nd$_{36}$Cu$_{64}$ thin films is presented in Fig. 7 as a function of $t$. The post-annealing temperature was 400°C. The thickness of the Nd$_{36}$Cu$_{64}$ layer was 0.5 nm. With increasing $t$, $H_{cj}$ increased and showed a maximum value of 19.5 kOe at $t = 8$ nm for the as-prepared film without annealing, and $H_{cj}$ of the post-annealed film exhibited a similar tendency. In contrast, $H_{cj}$ of the post-annealed Nd-Fe-B/Nd$_{36}$Cu$_{64}$ film exhibited extreme increases of approximately 5 kOe at every thickness. The film with the highest value of 26.1 kOe was obtained at $t = 8$ nm.

In order to clarify the effect of the Nd-Cu alloy cap layer on the Nd-Fe-B thin films with post-annealing on the improvement of $H_{cj}$, structural analysis and microstructural observation were performed. Figure 8 shows a cross-sectional HRTEM image of the Nd-Fe-B (30 nm)/Nd$_{36}$Cu$_{64}$ (0.5 nm) film with post-annealing. Three grains and their grain boundaries are evident in this figure. In the grain boundaries

![Fig. 6](image1.png)  
**Fig. 6** Magnetization curves of Nd-Fe-B (30 nm)/Nd-Cu (1 nm) thin films with different Cu concentrations x in the Nd$_{100-x}$Cu$_x$ layer, where x are (a) 0, (b) 18, (c) 64, (d) 78, and (e) 100 at.%. These films were post-annealed at 500 °C for 1 h. As a reference, the curves of the as-deposited Nd-Fe-B film without Nd-Cu are also presented in (f). Solid lines: $H \perp$ film plane, dashed lines: $H \parallel$ film plane.

![Fig. 7](image2.png)  
**Fig. 7** Effect of post-annealing on $H_{cj}$ for Nd-Fe-B and Nd-Fe-B/Nd$_{36}$Cu$_{64}$ thin films as a function of $t$. The symbols represent Nd-Fe-films with (open circles) and without (closed circles) post-annealing, and Nd-Fe-B/Nd$_{36}$Cu$_{64}$ films with post-annealing (open triangles).
between these grains, an amorphous structure with a thickness of approximately 1 nm was confirmed. The cross-sectional dark-field STEM image and EDS maps of each element for Nd-Fe-B (30 nm)/Nd_{36}Cu_{64} (1 nm) film before post-annealing are shown in Fig. 9. The Mo buffer layer, the Nd-Fe-B layer, and the Cr oxidation protection layer were observed in the STEM image. From the EDS maps, intense signals from Cr, Mo, and Cu were clearly detected at each layer. The Nd and Fe elements in the Nd-Fe-B layer showed a wide distribution in the Nd-Fe-B layer. The bright and dark contrasts in the Fe map correspond to the formation of the Nd_{2}Fe_{14}B and Nd_{1+},Fe_{4}B_{4} phases, as shown in Fig. 1.

For the Nd-Fe-B (30 nm)/Nd_{36}Cu_{64} (0.5 nm) film after post-annealing at 400°C for 1 h, the cross-sectional dark field STEM image and EDS maps of each element are shown in Fig. 10. Intense signals from a Mo buffer layer and a Cr protection layer were detected at the bottom and the top, respectively, of the Nd-Fe-B layer. On the other hand, the Cu element disappeared from the top of the layer after post-annealing, but appeared in the grain boundary between the Nd_{2}Fe_{14}B grains. On the grain boundary, the Nd element was slightly concentrated, and the Fe element was remarkably reduced. The reduction in the Fe concentration in the grain boundary of Nd-Fe-B grains provides a magnetically-decoupling of the Nd-Fe-B grains, which suppresses the domain wall motion in the magnetization reversal process. This result is in agreement with studies on the coercivity enhancement of nano-sized Nd-Fe-B powders by the diffusion of Nd-Cu\(^{(28)}\) or Nd-Cu-Al\(^{(29)}\) alloy. Therefore, the infiltration of non-magnetic elements into the grain boundary is an effective way to improve \(H_{CJ}\) because of the suppression of the exchange coupling between Nd_{2}Fe_{14}B grains.

4. Conclusion

In order to clarify the effect of the nano-grains and the grain boundaries of Nd-Fe-B magnets on the coercivity, ternary Nd-Fe-B thin films were formed by the direct-current (dc) magnetron sputtering method, and their structure and magnetic properties were investigated. The morphology of the films changed...
from an island structure to a continuous structure with increasing thickness (t), indicating that the magnetic state of the films shifted from single-domain particles to multi-domain particles with increasing t. The maximum coercivity ($H_{cJ}$) of the Nd-Fe-B thin films was 19.5 kOe at $t = 8$ nm, where the films were composed of both single-domain and multi-domain particles from the initial magnetization curve.\(^{(25)}\) When the effect of the infiltration of Nd-Cu into the Nd-Fe-B layer on the coercivity was investigated, $H_{cJ}$ showed a remarkable enhancement from 19.5 kOe to 26.1 kOe for the Nd-Fe-B (8 nm)/Nd$_{36}$Cu$_{64}$ (0.5 nm) films after the optimum post-annealing. Nd and Cu enrichment was clearly observed at the grain boundary of the Nd$_2$Fe$_{14}$B grains, whereas the concentration of Fe in the grain boundary phase decreased. This structural change, which suppresses the exchange coupling between Nd$_2$Fe$_{14}$B grains, provides the increase in $H_{cJ}$. These results suggest that controlling the nano-sized grain boundary through the infiltration of non-magnetic elements of Nd and Cu is extremely effective for improving the coercivity of Nd-Fe-B magnets.\(^{(26)}\)

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Reference


Figs. 1-5

Figs. 6-10

Takashi Sato
Research Fields:
- Hard Magnet
- Magnetic Thin Film
Academic Degree: Dr.Eng.
Academic Societies:
- The Magnetic Society of Japan
- The Japan Society of Applied Physics

Tetsu Ohsuna
Research Field:
- Electron Microscopy
Academic Degree: Dr.Eng.
Academic Societies:
- The Japan Institute of Metals
- The Japanese Society of Microscopy
- Japan Association of Zeolite

Yuji Kaneko
Research Field:
- Hard Magnet
Academic Degree: Dr.Eng.
Academic Societies:
- The Japan Institute of Metals
- The Japan Society of Powder and Powder Metallurgy
- The Japan Institute of Metals
Awards:
- The Japan Institute of Metals Technical Development Award, 1998
- Japan Society of Powder and Powder Metallurgy Award, 1998
Yukiko Takahashi*
Research Fields:
- Magnetic Thin Film
- Spintronics
- Transmission Electron Microscope
Academic Degree: Dr.Eng.
Academic Societies:
- The Magnetics Society of Japan
- The Japan Institute of Metals
- The Japan Society of Applied Physics
Awards:
- Oral Presentation Award, The Magnetic Society of Japan, 2004
- The Japan Institute of Metals Micrograph Award, 2005
- The Japan Institute of Metals Young Researcher Award (Materials Physics), 2006

Kazuhiro Hono*
Research Fields:
- Magnetic Material
- Spintronics
- Atom Probe Field Ion Microscope
- Transmission Electron Microscope
- Phase Transformations in Solids
Academic Degree: Ph.D.
Academic Societies:
- The Magnetics Society of Japan
- The Japan Institute of Metals
- IEEE Magnetic Society
- TMS
Awards:
- The Japan Institute of Metals Young Researcher Award, 1992
- The Japan Institute of Metals Meritorious Award, 1997
- Light Metal Advancement Award, The Japan Institute of Light Metals, 2003
- MSJ Outstanding Research Award, 2008
- TMS Fellows Award, 2011
- The Japan Institute of Metals Distinguished Contribution Award, 2011

Toshiyuki Shima**
Research Fields:
- Magnetic Material
- Thin Film
Academic Degree: Dr.Eng.
Academic Societies:
- The Magnetic Society of Japan
- The Japan Institute of Metals
- The Institute of Electrical Engineers of Japan
- IEEE
- Materials Research Society

*National Institute for Materials Science  
**Tohoku Gakuin University