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Preparation of Nd-Fe-B/α-Fe nano-composite thick-film magnets on various substrates using PLD with high laser energy density above 10 J/cm^2

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PLD (Pulsed Laser Deposition) method with high laser energy density (LED) above 10 J/cm^2 followed by a flash annealing enabled us to obtain isotropic nano-composite thick-film magnets with $(BH)_{max}$ ≧ 80 kJ/m^3 on polycrystalline Ta substrates. We also have demonstrated that a dispersed structure composed of α-Fe together with $Nd_2Fe_{14}B$ phases with the average grain diameter of approximately 20 nm could be formed on the Ta substrates. In this study, we tried to enhance the $(BH)_{max}$ value by controlling the microstructure due to the usage of different metal based substrates with each high melting point such as Ti, Nb, and W. Although it was difficult to vary the microstructure and to improve the magnetic properties of the films deposited on the substrates, we confirmed that isotropic thick-film magnets with $(BH)_{max}$ ≧ 80 kJ/m^3 based on the nano-dispersed α-Fe and $Nd_2Fe_{14}B$ phases could be obtained on various metal substrates with totally different polycrystalline structure. On the other hand, the use of a glass substrate lead to the deterioration of magnetic properties of a film prepared using the same preparation process.
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I. INTRODUCTION

A permanent film magnet is a promising material to develop various industrial and medical fields.[1–3] For example, Nd-Fe-B film magnets thicker than 10 μm on metal substrates and metal buffer layers prepared using a sputtering method have been applied to miniaturized electronic devices.[4,5] A friction drive small motor comprising a PLD (Pulsed Laser Deposition)-fabricated isotropic Nd-Fe-B thick film on a Ta substrate was demonstrated by our group.[6]

Recently, we enhanced $(BH)_{max}$ value of an isotropic Nd-Fe-B film magnet deposited on a Ta substrate by taking account of the PLD method using the small spot size of laser beam less than 1 mm together with LED (Laser Energy Density) ≧ 10 J/cm^2.[7] The value of $(BH)_{max}$ ≧ 80 kJ/m^3 is attributed to the microstructure of $Nd_2Fe_{14}B$ + α-Fe nano-composite dispersed structure with refined grain through the deposition followed by a flash annealing process.[8] The observation of microstructure also revealed that the as-deposited films had a columnar structure with the width less than 50 nm composed of α-Fe together with amorphous Nd-Fe-B phases as shown in Figs. 1(a) and 1(b). Although the mechanism of the above-mentioned phenomenon isn't still clear, we have demonstrated that PLD with LED ≧ 10 J/cm^2 provided the interesting and reproducible phenomenon. Not only control of the

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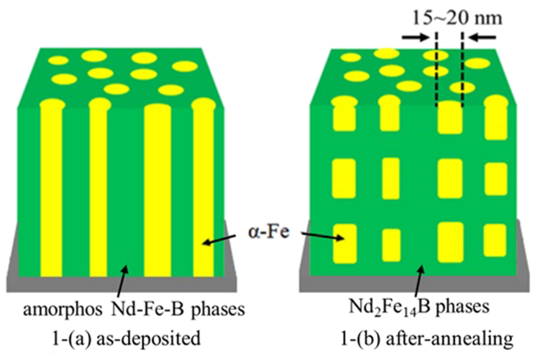
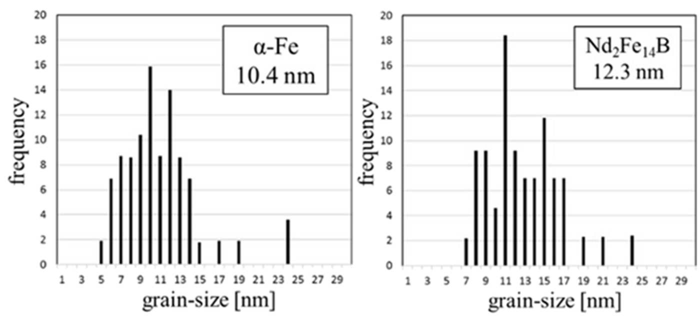


(a) Schematic diagram of the cross-sectional microstructure of as-deposited 1-(a) and annealed 1-(b) films prepared on Ta substrates using LED ≧ 10 J/cm^2.



(b) Distribution of grain diameter of α-Fe and $Nd_2Fe_{14}B$ phases in a nano-composite film magnet after a flash annealing process. (see FIG. 1. 1-(b)) The film was prepared on a Ta substrate using LED ≧ 10 J/cm^2.

FIG. 1. Microstructures of an as-deposited (1-(a)) and an anneled (1-(b) and (b)) film magnets prepared on a Ta substrate using LED ≧ 10 J/cm^2, respectively.

as-deposited nanostructure but also the transformation through the annealing process is indispensable to achieve good magnetic properties, however the microstructure and magnetic properties have been confirmed only on a Ta substrate.

In this paper, we tried to enhance the $(BH)_{max}$ value by taking account of the effect of substrate materials on the microstructure because the value was inferior to those of isotropic RE (Nd or Pr)-Fe-B/α-Fe nano-composite ribbons with $(BH)_{max}$ above 130 kJ/m^3.[9,10] Namely, preparation of isotropic Nd-Fe-B thick-films on various metal substrates such as Ti, Nb, and W was carried out in the above-mentioned PLD with LED ≧ 10 J/cm^2. In order to prepare Nd-Fe-B films using a sputtering method, a lot of researchers have already used these refractory metals as substrates and buffer layers.[11–13] This contribution reports the magnetic properties together with the microstructure in the PLD-fabricated thick-films on metal substrates with various polycrystalline structures. Resultantly, it was found that LED ≧ 10 J/cm^2 is a dominant condition to form the above-mentioned transformation on those metal substrates. In addition, we tried to prepare the films deposited on glass substrates in order to apply the samples for MEMS (Micro Electro Mechanical Systems).[14]

II. EXPERIMENTAL PROCEDURE

A rotated $Nd_{2.6}Fe_{14}B$ target was ablated using an Nd-YAG pulse laser with LED ≧ 10 J/cm^2. The deposition rate was approximately 15 μm/h. All the as-deposited films were annealed by a flash annealing method to form $Nd_2Fe_{14}B$ crystalline phase.[15] In the experiment, refractory metal based substrates (Ta, Ti, Nb, W) were used in order to suppress the diffusion of elements from each substrate to a film during the annealing process. Figure 2 shows the X-ray diffraction patterns of the metal based substrates which had a polycrystalline structure with various planes. Furthermore, a glass substrate (TEMPAX Float, Schott AG: 5 mm × 5 mm square) was used as a substrate. The composition of all

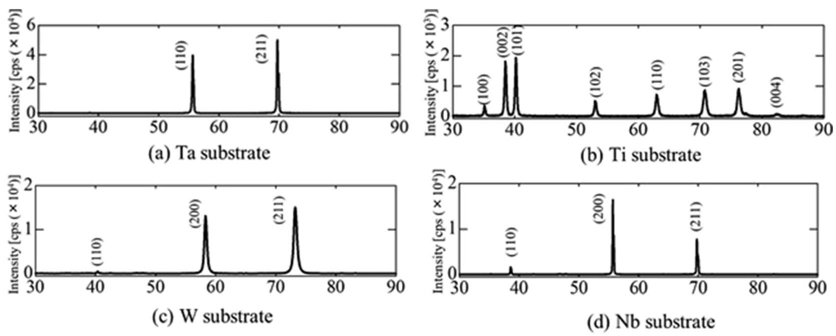


FIG. 2. X-ray diffraction patterns of refractory metal based substrates seen in (a), (b), (c) and (d). The substrates had a polycrystalline structure with various planes.

the films was measured with a SEM-EDX and the magnetic properties were measured with a vibrating sample magnetometer (VSM), respectively. The crystal structure together with micro structure of each film were observed with an X-ray diffraction (XRD) meter and a transmission electron microscope (TEM).

III. RESULTS AND DISCUSSION

A. Magnetic properties and microstructure of Nd-Fe-B films prepared on various metal substrates using LED ≧ 10 J/cm^2

Figure 3 shows the $(BH)_{max}$ values of Nd-Fe-B films deposited on various metal substrates using LED ≧10 J/cm^2 followed by a flash annealing. Each average $(BH)_{max}$ value plotted as "○" was calculated by using the values of 4 - 10 samples. Although it was difficult to increase the $(BH)_{max}$ of the annealed films, almost all the average ones exceeded 80 kJ/m^3. Observation on crystalline structure of the as-deposited samples on the substrates indicated the existence of diffraction peaks corresponding to α-Fe phase (2θ: 44° and 82°) due to the precipitation of α-Fe as reported in Refs. 7 and 8. In the present stage, we don't understand the mechanism about the difference in intensities for the Fe peaks on XRD when the Nd-Fe-B films are a produced on different substrates. We need to investigate the phenomenon as a future work. The both α-Fe and $Nd_2Fe_{14}B$ phases could be observed in all the annealed samples deposited on several metal substrates.

Figure 4 shows TEM observations of the samples deposited on Ta, Ti, W, and Nb substrates. The microstructure of as-deposited together with annealed samples had similar tendency. We considered that the relatively high $(BH)_{max}$ values shown in Fig. 3 are attributed to the transformation from the columnar structure to dispersed one through the annealing process. (see Fig. 1) It was clarified that

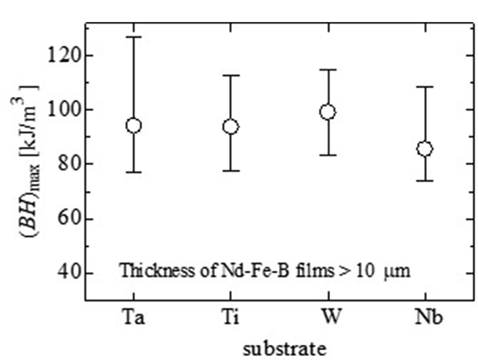


FIG. 3. $(BH)_{max}$ of annealed Nd-Fe-B films thicker than 10 μm deposited on various metal substrates using LED ≧ 10 J/cm^2. Each average $(BH)_{max}$ value plotted as "○" was calculated by using the values of 4 - 10 samples.

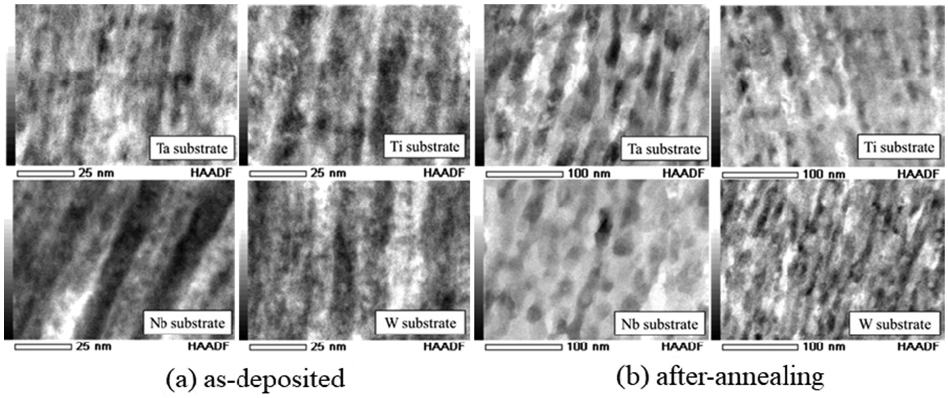


FIG. 4. Microstructure of as-deposited (a) and an annealed (b) film magnets deposited on various substrates using LED≧ 10 J/cm^2. In all the as deposited samples, a columnar structure could be observed. Furtheremore, all the annealed samples had a dispersed structure.

the microstructure could be formed on various metal substrates with different polycrystalline phases displayed in Fig. 2. These results suggest that the deposition condition such as LED ≧ 10 J/cm^2 is more important compared to the selection of refractory metal based substrates.

B. Investigation on the degraded behavior of Nd-Fe-B films prepared on glass substrates using LED ≧ 10 J/cm^2

We also have reported the preparation of film magnets thicker than 10 μm on a glass substrate in order to apply them to MEMS.[14] In the section, an investigation on several properties of the films deposited on glass substrates using LED ≧ 10 J/cm^2 was carried out. Figure 5 shows relationship between $(BH)_{max}$ and the Nd contents (Nd/(Nd+Fe)) in the films deposited on Ta and glass substrates, respectively. The Nd contents of films prepared on Ta substrates varied from 10 to 13.5 at. %, which was smaller by several at. % than that of a target composition. It was confirmed that the similar tendency was also observed in the films deposited on Ti, W, and Nb substrates. The reduction in Nd between a film and a target is considered to be attributed that Fe atoms tend to move directly to the substrates and Nd atoms tend to be widely emitted under the explosive deposition process using LED ≧ 10 J/cm^2 as explained in the previous paper.[7,8] On the other hand, the values of Nd/(Nd+Fe) of films deposited on glass substrates varied from 13.5 and 15.0 at. %. In the case of the samples fabricated on

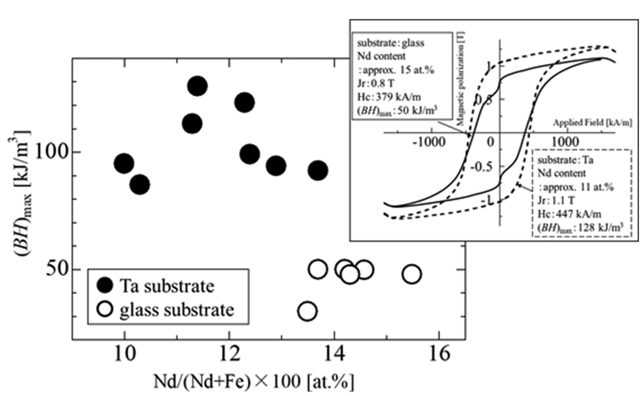


FIG. 5. $(BH)_{max}$ as a function of the Nd contents (Nd/(Nd+Fe)) in the films deposited on Ta and glass substrates, respectively. The reduction in $(BH)_{max}$ together with Nd contents occurred in the films deposited on glass substrates compared to those of samples prepared on Ta substrates. The inset shows J-H loops of the samples deposited on a Ta and a glass substrate, respectively. The residual magnetization of the sample on a glass substrate was lower than that of another one.

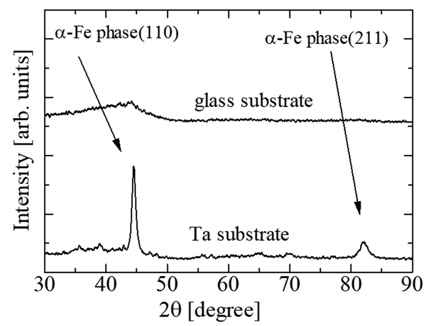


FIG. 6. X-ray diffraction patterns of as-deposited films deposited on glass and Ta substrates, respectively.

glass substrates, not only α-Fe crystalline peaks in the as-deposited sample but also nano-composite structure after the annealing process couldn't be confirmed as shown in Fig. 6. The inset of Fig. 5 shows the comparison of two J-H loops for the samples deposited on a Ta and a glass substrate, respectively. In the case of a sample deposited on a glass one, the maximum magnetic polarization applied at the magnetic field of approximately 1600 kA/m together with the residual magnetic polarization were lower than that of another one because the Nd amount of a sample deposited on a glass substrate was larger than that of a sample on a Ta substrate. Namely, it was difficult to obtain a nano-composite magnet film on a glass substrate. Although it was considered that there are two phases with high coercivity ($Nd_2Fe_{14}B$ phase) and low one, we can't find the low coercivity phase in the present stage. A further investigation on the existence of the low coercivity phase is required. Consequently, the use of a glass substrate isn't suitable to prepare a nano-composite Nd-Fe-B/α-Fe film magnet with $(BH)_{max} \geqq 80$ kJ/m^3 by using a high LED.

IV. CONCLUSION

In this study, we investigated the effect of metal substrates with a high melting point on the microstructure and magnetic properties of isotropic nano-composite thick-film magnets prepared using a PLD with LED $\geqq$ 10 J/cm^2 followed by a flash annealing. Furthermore, we also tried to obtain the above-mentioned film magnet on glass substrates using the preparation process from a MEMS application point of view. The obtained results are summarized as follows;

(1) The dispersed structure composed of α-Fe together with $Nd_2Fe_{14}B$ phases with the average grain diameter of approximately 20 nm could be formed on various refractory metal based substrates such as Ta, Ti, Nb, and W.

(2) It was found that there was a difference in Nd levels in the glass films compared to those deposited on the metal substrates. We had difficulty in obtaining the above-mentioned transformation of a film deposited on a glass substrate.

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