Microstructure characterization of high-energy product Nd-Fe-B thin film

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Abstract: A Si/Mo(50 nm)/Nd-Fe-B(400 nm)/Mo(50 nm) film with relatively high-energy product \( (BH)_{\text{max},
\perp} = 247 \text{ kJ/m}^3 \) was prepared on a Si substrate heated at 650 °C. The microstructure of the film was investigated by X-ray diffractionometry (XRD) and high-resolution transmission electron microscopy (HRTEM). The Nd-Fe-B thin film shows a notable out-of-plane \( c \)-axis texture. The \( (110) \) orientated Mo grains is proved to promote the growth of \( c \)-axis oriented texture of the \( \text{Nd}_2\text{Fe}_{14}B \) grains, which is favorable to achieve a high remanence. Nano-scale spherical Nd-O phases composed of randomly orientated polycrystalline grains and a sharp grain boundary without grain boundary phase between two \( \text{Nd}_2\text{Fe}_{14}B \) grains are observed. The coercivity highly depends on a certain amount of Nd-O phase and interface morphology.

Key words: Nd-Fe-B thin films; microstructure; Nd-O phase; magnetic properties

1 Introduction

Anisotropic Nd-Fe-B thin films have received considerable attention in recent years because of their potential applications in micromagnetic devices, micromechanical devices and magnetic recording media[1–2]. It is known that the magnetic properties of Nd-Fe-B magnet are highly sensitive to its microstructure. In bulk materials, the microstructure consisting of a uniform distribution of aligned \( \text{Nd}_2\text{Fe}_{14}B \) grains surrounded by a non-magnetic Nd-rich grain boundary phase is desired for high performance[3–4]. For thin films, fine microstructure[5–6] as well as out-of-plane texture[7] is needed to achieve high energy product. Sputtering is one of the feasible ways to prepare anisotropic Nd-Fe-B thin films. During the sputtering, the microstructure and texture of the \( \text{Nd}_2\text{Fe}_{14}B \) phase are affected by a number of processing parameters, such as vacuum condition, deposition temperature, buffer layer, and deposition rate[8–18]. Nd-Fe-B films deposited on Si substrate are usually with a sandwiched structure. First, a thin layer of Mo or Ta (about 50 nm in thickness) is deposited on the substrate as the buffer layer. The buffer layer promotes the out-of-plane texture of the Nd-Fe-B film and acts as a barrier to prevent diffusion of the substrate materials into the film[19]. Then the Nd-Fe-B film is deposited. Out-of-plane texture is formed either by a direct crystallization on a heated substrate or by a post-deposition annealing. Finally, a cap layer which protects the film from oxidation is deposited. According to the available reports, the microstructure of Nd-Fe-B film is highly different from its bulk counterpart, which is highly sensitive to the processing parameters. Therefore, it is of crucial importance to understand the relationship among the processing parameters, microstructure and magnetic properties of Nd-Fe-B thin films.

In this work, an Nd-Fe-B film Si/Mo(50 nm)/Nd-Fe-B(400 nm)/Mo(50 nm) showing a relatively high-energy product \( (BH)_{\text{max},
\perp} = 247 \text{ kJ/m}^3 \) was prepared under the condition that the substrate temperature \( T_s \) was higher than the crystallization temperature \( T_c \) of the \( \text{Nd}_2\text{Fe}_{14}B \) phase. The microstructure characteristics of the film, such as texture, interface morphology, grain structure and local chemistry of the grains were investigated.

2 Experimental

Nd-Fe-B films were prepared by sputtering a piece of \( \text{Nd}_{14}\text{Dy}_1\text{Fe}_{68}\text{Co}_{10}\text{B}_7 \) target in a high vacuum chamber
equipped with multi-sputtering guns. A commercial Mo target of 99.9% purity was used for depositing the buffer and cap layers. The initial pressure of the chamber was better than $1.5 \times 10^{-5}$ Pa and the Ar gas pressure was kept at 0.7 Pa during direct current sputtering. A film Si/Mo(50 nm)/Nd-Fe-B(400 nm)/Mo(50 nm) was deposited on a Si (100) substrate that was heated up to 650 °C. No post-deposition annealing was carried out.

The magnetic properties of the as-deposited film were measured at room temperature using a Quantum Design MPMS-7S superconducting quantum interference device (SQUID). Crystalline structure of the film was characterized by X-ray diffraction (XRD) with the Cu Kα radiation. The cross-sectional specimens for transmission electron microscopy (TEM) investigation were prepared by gluing two pieces of films face to face. Then a thin slice was cut perpendicular to the gluing plane and mechanically polished to about 80 μm. The specimen was dimpled from one side and finally ion-milled using Gatan 691 Precision Ion Polishing System. The cross-sectional microstructures of the films were examined by HRTEM (JEOL JEM-2100F) operating at 200 kV. The chemical compositions of local regions in the microstructure of the thin film were analyzed by EDS equipped in the TEM.

3 Results and discussion

Magnetic properties measurements perpendicular to the film plane indicated that the film exhibited a remanence of $B_r = 1.17$ T and a coercivity of $H_c = 1090$ kA/m. The energy product was measured to be 247 kJ/m³.

XRD pattern of the Si/Mo(50 nm)/Nd-Fe-B(400 nm)/Mo(50 nm) film shows that the film is in a well crystallized state (see Fig.1). Apart from the major Nd$_2$Fe$_{14}$B phase, trace of the Nd-rich phase is found in the XRD pattern. Diffractions from Si substrate and Mo are also found. The (105) diffraction is the strongest peak for the Nd$_2$Fe$_{14}$B phase in the film. This indicates a notable c-axis texture for the Nd$_2$Fe$_{14}$B phase since the (105) plane is about 15° from the c-plane. Moreover, there exists a certain amount of the Nd-O phase in the film. The strongest peak for Mo is (110), which may indicate a preferred orientation for the buffer layer.

Fig.2(a) shows a cross-sectional TEM image of the Nd-Fe-B thin film observed under the edge-on condition. The Nd-Fe-B layer is encapsulated between the Mo buffer layer and cap layer. The film thickness is about 350 to 400 nm. It is found that some nano-scale spherical particles are embedded in the film. Composition analysis using a beam size of about 1 nm indicates that these spherical particles are rich in Nd and O (see Table 1). Thus they are most probably the Nd-O phase. The O

![Fig.1 XRD pattern of Si/Mo(50 nm)/Nd-Fe-B(400 nm)/Mo(50 nm) film](image1)

Table 1 Typical compositions of points A, B and C shown in Fig.2 determined by EDS (mole fraction, %)

<table>
<thead>
<tr>
<th>Point</th>
<th>Nd</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>13</td>
<td>83</td>
<td>4</td>
</tr>
<tr>
<td>B</td>
<td>37</td>
<td>10</td>
<td>53</td>
</tr>
<tr>
<td>C</td>
<td>36</td>
<td>27</td>
<td>37</td>
</tr>
</tbody>
</table>
content in the matrix phase is quite low (see Table 1) and the Fe/Nd ratio is close to 7, indicating that it is the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phase. Fig.2(b) shows a HRTEM image of a boundary at the edge of a columnar \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grain whose longitude direction is almost parallel to film normal. Both the selected-area diffraction pattern and the characteristic lattice spacing 1.22 nm clearly indicate that the \( c \)-axis of the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grain is perpendicular to the edge. TÉNAUD et al[20] and ZOU[21] showed that the easy growth axis of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) crystal corresponded to the \( a \)-axis of the tetragonal structure, which is perpendicular to \( c \)-axis of magnetization. However, such a preferred growth orientation is unfavorable to achieve a high-energy product \( \text{Nd}-\text{Fe-B} \) thin film. SERRONA et al[22] suggested that if the \( c \)-axis of the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains could be aligned parallel to the film normal, the \( \text{Nd}-\text{Fe-B} \) thin film would exhibit high remanence and high coercivity.

Fig.3 shows the interface regions between the Nd-Fe-B layer and the Mo buffer layer (see Fig.3(a)), the Mo buffer layer and the Si substrate (see Fig.3(b)), respectively. In Fig.3(a), the lattice image shows that the (001) plane of the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grain is about 15° to the film plane, which is well consistent with the XRD analysis. A thin amorphous \( \text{SiO}_2 \) layer about 3 nm in thickness can be observed between the Si substrate and the Mo buffer layer (see Fig.3(b)). Fast-Fourier-Transforms from the lattice image indicate that the (110) plane of the Mo buffer layer is parallel to the (100) plane of the Si substrate. This coincides with the strong (110) peak from Mo in the XRD pattern (see Fig.1). For BCC metal, (110) plane is the close-packed plane of Mo and should be the preferred growth orientation during deposition. Taking the lattice constants of Mo and \( \text{Nd}_2\text{Fe}_{14}\text{B} \) into consideration, if the (110) plane of Mo is parallel to the (001) plane of \( \text{Nd}_2\text{Fe}_{14}\text{B} \), the maximum lattice misfit between the two lattices is around 6%. This may explain the fact that a (110) orientation-textured Mo layer promotes the growth of \( c \)-axis oriented texture of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) layer, where the \( c \) axis is normal to the film plane.

In the bulk \( \text{Nd}-\text{Fe-B} \) magnet, the Nd-O phase is mostly in the form of thin film at the grain boundary of the matrix phase. In the \( \text{Nd}-\text{Fe-B} \) thin film, most of the Nd-O phase is in the form of spherical particles embedded in the matrix (see Fig.4). This is in agreement with previous reports[17]. Fig.4(b) shows a sharp grain boundary without grain boundary phase between two \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains in the film. There is a broad amorphous region between the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) matrix and the Nd-O particle (see Fig.4(c)). The HRTEM image of the Nd-O phase indicates that the spherical Nd-O phase is composed of randomly orientated grains less than 10 nm (see Fig.4(d)). The corresponding diffraction pattern is typically polycrystalline.

Our present investigation revealed that the phase constitution of the \( \text{Nd}-\text{Fe-B} \) thin film was almost the same as its bulk counterpart. However, the microstructure of \( \text{Nd}-\text{Fe-B} \) thin film shows some unique features that differ from the bulk material. For high-energy product \( \text{Nd}-\text{Fe-B} \) thin films, high anisotropy after crystallization is essential for achieving a high remanence. Since the preferred growth direction of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) crystal is perpendicular to its easy axis of magnetization, the role of buffer layer is of crucial importance. It is deduced from XRD analysis and has been shown in the present work that the (110) oriented Mo layer promotes the growth of (001) textured \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains. Depending on the deposition rate, the deposited \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains are either equi-axised or columnar. Columnar \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains are preferred to achieve high energy product. Thus a high deposition rate is needed to ensure a columnar growth of the \( \text{Nd}_2\text{Fe}_{14}\text{B} \) grains whose (001) plane is perpendicular to the growth direction (film normal) (see Fig.5). Besides the highly
textured Nd$_2$Fe$_{14}$B matrix grains, a non-magnetic phase usually the Nd-O phase that separates the Nd$_2$Fe$_{14}$B grains is needed for a high coercivity. In the bulk materials, a certain amount of oxygen and smooth interfaces are an indispensable ingredient to achieve a high coercivity. There are at least two main sources to enroll oxygen into the Nd-Fe-B thin film. First of all, there must be certain Nd-rich phase in the sputtering target. Secondly, the residual oxygen in the high vacuum chamber is inevitable. However, the Nd-O phase in the thin film is in the form of particles consisting of randomly orientated nano-scale crystals. The mechanism of the effect of these spherical Nd-O particles on magnetic properties is a subject for further investigation. An proposed model of high-energy product Nd-Fe-B thin film is summarized in Fig.5.

4 Conclusions

The Si/Mo(50 nm)/Nd-Fe-B(400 nm)/Mo(50 nm) film with $B_r=1.17$ T, $H_{ic}=1,090$ kA/m and $(BH)_{max}=247$ kJ/m$^3$ was prepared. XRD measurement confirmed the c-axis out-of-plane texture of the Nd$_2$Fe$_{14}$B phase. (110) oriented Mo grains are found to promote the growth of c-axis texture of the Nd$_2$Fe$_{14}$B phase. Unlike bulk material, the Nd-O phase is in the form of spherical particles in the film. HRTEM indicated
that these Nd-O particles were composed of randomly orientated polycrystalline grains. The grain boundary between two Nd$_2$Fe$_{14}$B grains is considerably sharp without any indication of a grain boundary phase. A high anisotropy of Nd$_2$Fe$_{14}$B phase and a certain amount of Nd-O phase in the thin film correspond to high magnetic properties.

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References