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Effects of underlayer materials and substrate temperatures on the structural and magnetic properties of $Nd_2Fe_{14}B$ films

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Thin films of $Nd_2Fe_{14}B$ were fabricated on heated glass substrates by dc magnetron sputtering. Different material underlayers (Ta, Mo, or W) were used to examine the underlayer influence on the structural and magnetic properties of the NdFeB films. Deposited on a Ta buffer layer at 420°C, the 300 nm thick NdFeB films were shown to be isotropic. But when the substrate temperature T_s was elevated to 520°C, the $Nd_2Fe_{14}B$ crystallites of (00l) plane were epitaxially grown on Ta (110) underlayer. In contrast, Mo (110) buffer layer could not induce any preferential orientation in NdFeB film irrespective of the substrate temperature or film thickness. The W buffer layer was found to be most effective for the nucleation of $Nd_2Fe_{14}B$ crystallites with c-axis alignment perpendicular to the film plane when $T_s < 490$°C. But at T_s=490°C the magnetic layer became isotropic. The maximum coercivity obtained was about 995 kA/m for the 100nm film deposited on W underlayer at 490°C. These variations were tentatively explained in terms of the lattice misfit between the underlayer and the magnetic layer, combined with the considerations of underlayer morphologies.

Keywords: $Nd_2Fe_{14}B$ film, underlayer, substrate temperature, texture
PACC: 7570, 7550V, 7550B

1. Introduction

NdFeB film is one of the promising candidates in the applications of micromechanical devices, such as micromotors and actuators. Since Cadieu *et al*[1] reported that textured 2:14:1 phase could be produced by sputtering in 1986, a great deal of work has been done to understand the physical mechanisms and improve the magnetic performance of NdFeB films. Parts of these efforts are concentrated on finding a proper underlayer material to promote the texture of magnetic layers as well as to prevent neodymium from oxidization. Keavney *et al*[2] reported that NdFeB thin films with a c-axis orientation and bulk-like magnetic properties were fabricated on Mo (100) buffer layers. Mapps *et al*[3] found that Pt (111) layer was effective to grow NdFeB films with a good perpendicular magnetic anisotropy. Recently, Hannemann *et al*[4] successfully fabricated NdFeB films on Ta (110) buffer layer on single crystalline Al_2O_3 (0001) substrates by pulsed laser depositions and a prominent perpendicular magnetic anisotropy was observed.

In this work, NdFeB films are deposited on Ta, Mo and W underlayers, separately. The results are discussed according to the epitaxial relation and the physical process of magnetization reversal.

2. Experiment

The films M(5 nm)/NdFeB/M(100nm) (M=Ta, Mo, or W) are deposited on glass substrates by dc magnetron sputtering. The magnetic Nd–Fe–B films are deposited by using a composite target, which is composed of an iron plate with Nd chips and B flakes uniformly placed on it. The base pressure before introducing Ar is below 8×10^{-5}Pa. The sputtering pressures for the underlayer and the magnetic layer are 0.7Pa and 0.4Pa, respectively. The chemical composition of the films is analysed by electron probe microanalyser (EPMA) with an error smaller than 0.1 at%, and controlled to achieve the ratio of Nd:Fe:B=19:73:8. Film thickness is measured by a

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surface texture system. The phase structures of the samples are identified using an x-ray diffractometer (XRD) with Cu Kα radiation. Scanning electron microscope (SEM) and atomic force microscope (AFM) are used to characterize the morphological features of the films. The magnetic properties of the samples are measured by a vibrating sample magnetometer (VSM) with a maximum applied field of 1200kA/m.

NdFeB films with the three kinds of underlayers have been investigated in a wide range of deposition temperature, from room temperature to 650°C. The change of structural and magnetic properties of these films is very distinct. In the following, some representative deposition temperatures are selected to discuss the influence of underlayer materials on the structural and magnetic properties of NdFeB films.

3. Results

Table 1 summarizes the preparation conditions and magnetic properties of some selected NdFeB films deposited on Ta, Mo and W underlayers. The average grain size $< D >$ was estimated from the SEM images of these films. The roughness Ra was measured by AFM. For comparison, we also give the parameters of the NdFeB film without a buffer layer. It is evident that a buffer layer is critically needed to guarantee the hard magnetism of the NdFeB films prepared. With a buffer layer, large coercivity can be obtained in the films deposited even at 420°C, and it is enhanced with increasing substrate temperature T_s. However, the buffer layers may affect the magnetic properties differently, showing a combined effect of the materials of buffer layer and substrate temperature. When deposited on Ta layer at $T_s < 520$°C, the in-plane coercivity $H_{c//}$ and remanent magnetization ratio $S_{//}$ are both larger than their out-of-plane counterparts by a certain amount. But, the situation reverses if T_s is elevated to more than 520°C. This means that the easy direction of the magnetic anisotropy rotates at a higher deposition temperature, and more of the hard magnetic phase will be aligned perpendicularly to the film plane. In the case of Mo buffer layer, with rising T_s the coercivity of the NdFeB films increases significantly, indicating an improvement of the crystallization condition for the 2:14:1 phase. At 520°C, the coercivity in both directions reaches 796kA/m. The same values in the two directions imply the isotropic magnetic properties of the film. This is generally found in the films deposited on Mo underlayer in this work. However, it is interesting to find that the NdFeB films on W underlayer show an opposite magnetic anisotropy compared with the films deposited on Ta underlayer at low temperatures. The film prepared on W underlayer has a prominent perpendicular magnetic anisotropy. But it disappears at $T_s > 490$°C, and the film becomes magnetically isotropic.

Table 1. Magnetic properties and average particle size of $Nd_2Fe_{14}B$ films with different thicknesses deposited on Ta, Mo and W underlayers, at different substrate temperatures.

underlayer	T_s/°C	δ/nm	$H_{c\perp}$/(kA·m^{-1})	$H_{c//}$/(kA·m^{-1})	$S_\perp$	$S_{//}$	$< D >$/nm	Ra/nm
none	420	300	245	40	0.4	0.47	–	–
Ta	420	300	362	414	0.57	0.83	291	11.4
	490	300	342	493	0.5	0.70	551	58.2
	520	300	533	279	0.78	0.5	–	113.1
Mo	420	100	422	406	0.63	0.65	217	6.5
	490	100	661	780	0.9	0.66	305	10.7
	520	100	828	812	0.87	0.66	–	16.9
W	420	100	509	271	0.85	0.26	176	5.2
	490	100	748	995	0.8	0.75	321	20.3

Figure 1 shows the XRD patterns of NdFeB films deposited on Ta, Mo and W underlayers at the representative temperatures. In Fig.1, only peaks from the tetragonal 2:14:1 phase are observed in the deposition temperature range of 420–520°C in addition to the (110) peaks from the individual buffer layer. For the film deposited on Ta layer at 420°C, the lines of (204), (214), (313), (224) and (314) appear clearly with similar intensities, indicating a random distribution of c-axis of the 2:14:1 phase (Fig.1 (a)). But at 520°C, the lines of (00l) and (105) becomes intense and dominant, compared with the less intense (214) and (313) lines, implying that the c-axis in most grains tends to be perpendicularly aligned (Fig.1 (b)). For the films deposited on Mo layer, diffraction lines with various crystallographic orientations are observed in

the whole temperature range (Figs.1(c) and 1(d)). No preferential texture can be found for films deposited on Mo underlayer. But when W buffer layer is used, the case is different. Only $(00l)$ diffraction lines with a less intense (105) peak are found for the films deposited on W layer at 420°C, while for deposition at 490°C, (204), (215), (105) and (314) peaks are seen with similar intensities. This means that the $(00l)$ texture in the 2:14:1 phase can form and retain at a substrate temperature below 490°C, but it will be destroyed at higher temperatures. The XRD analysis for all the samples is consistent with their corresponding magnetic properties (see Table 1).

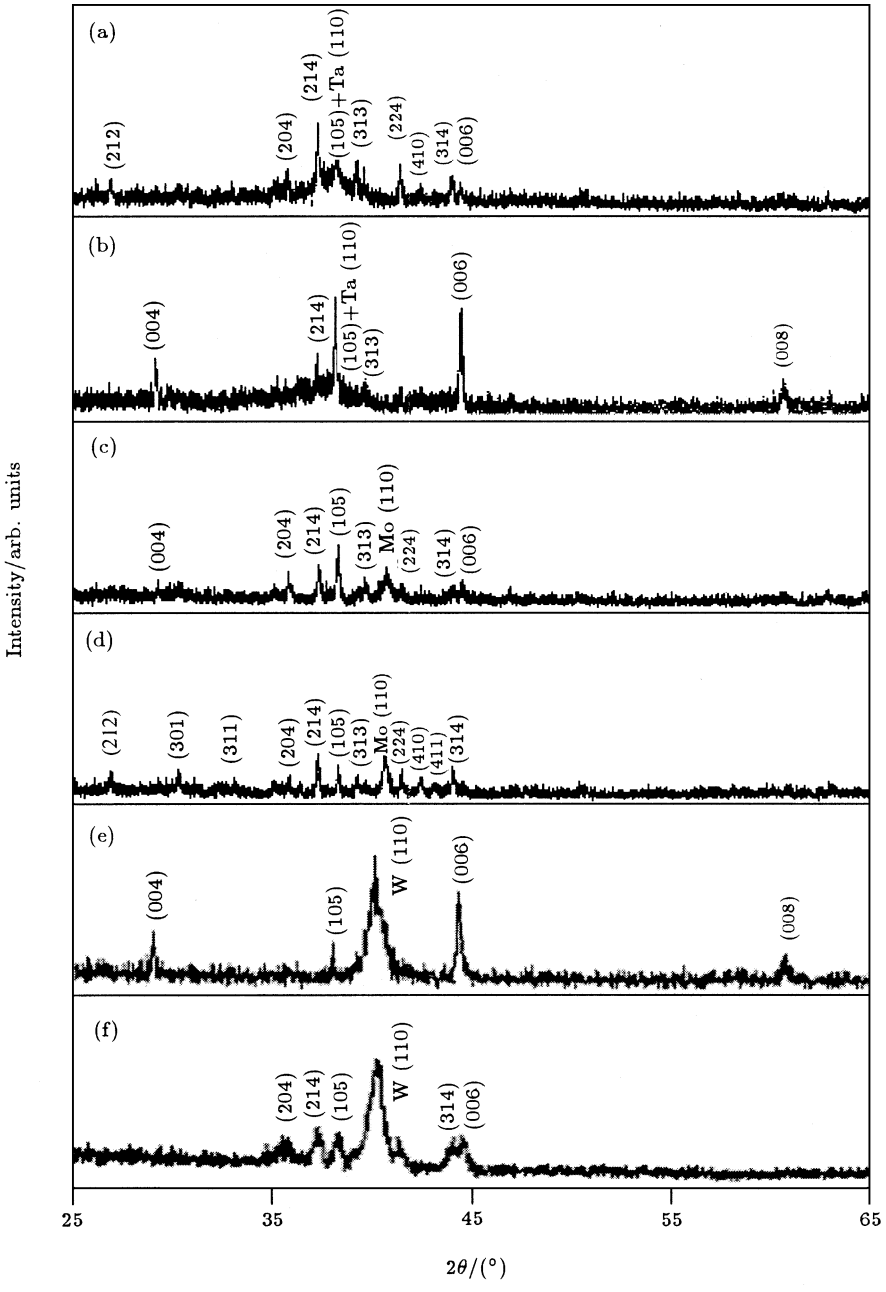


Fig.1. The XRD patterns of $Nd_2Fe_{14}B$ films deposited on Ta buffer layer at 420°C (a) and 520°C (b); Mo buffer layer at 420°C (c) and 520°C (d); and W buffer layer at 420°C (e) and 490°C (f).

The morphologies of NdFeB films are characterized using SEM and AFM images. Grain sizes depend on deposition temperature, and increase rapidly with rising temperature. As shown in Table 1, $< D >$ is much larger than that calculated from the broadness of XRD lines according to the Scherrer formula, which

is in the range of 20–30nm. Therefore, it is believed that a large number of tiny crystallites may form a cluster. Figure 2 shows the SEM images of NdFeB films deposited on Ta layer at 520°C (a), Mo layer at 520°C (b), and W layer at 420°C (c). The morphologies in the three cases are obviously different. Large homogeneous local regions are found in Fig.2(a), accompanied by big holes and some tiny grains distributed on the film surface. It is likely that the film forms a columnar structure on the Ta buffer layer, and some of the columns become connected at a certain film thickness less than 300nm. Compared with this, the films on Mo and W layers are granular-structured and consist of large particles. As shown in the figure, particles grown on Mo layer are of platelet shape more or less titling up from the film plane, while those on W layer are ellipse-like along the film thickness direction. This may be one of the reasons accounting for the different magnetic properties of the two films. In Fig.2(b), there also are certain unknown tiny grains with different compositions based on their brightness. They are tentatively assumed to be Nd and/or B precipitates because their contents in the films are higher than the stoichiometric ratio of 2:14:1.

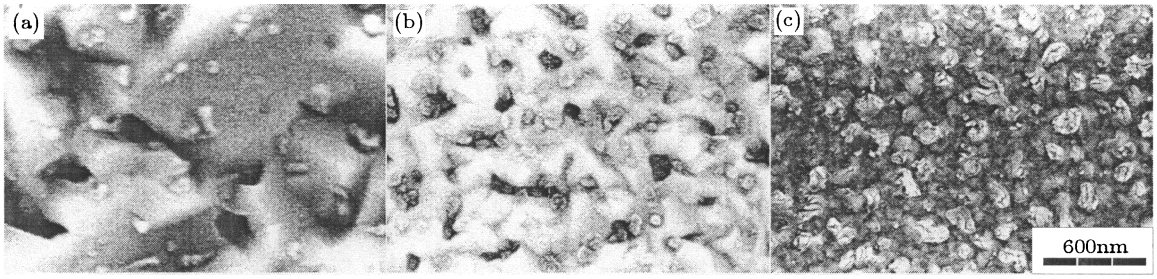


Fig.2. Plane-view SEM images of $Nd_2Fe_{14}B$ films deposited on Ta layer at 520°C (a), Mo layer at 520°C (b), and W layer at 420°C (c).

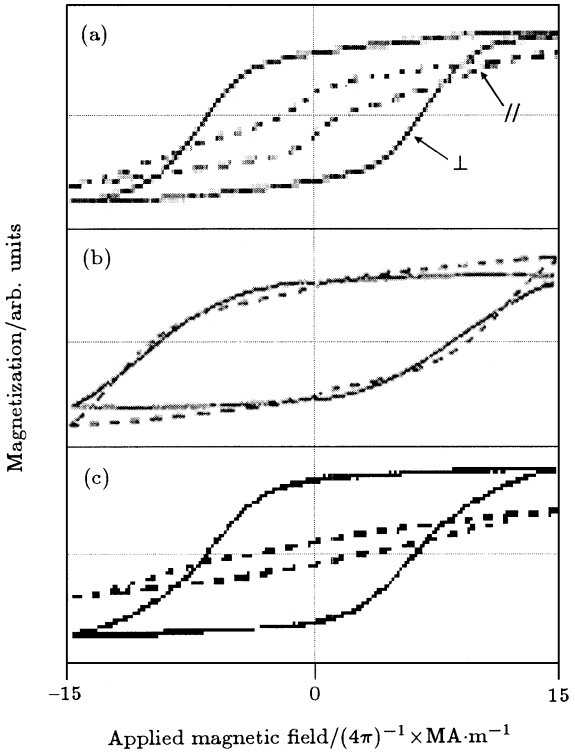


Fig.3. Hysteresis loops of the samples shown in Fig.2.

Figure 3 shows the typical hysteresis loops of the samples given in Fig.2. The demagnetization effect is not corrected in these curves. It is difficult to determine the effective demagnetization factor $N_{\rm eff}$, since the microstructure consists of many irregular-shaped grains which may be partially decoupled magnetically; flux closure can occur not only at the edges of the films, but also within the films. From Figs.3(a) and 3(c), it is obvious that the films on Ta and W layers have a well perpendicular magnetic anisotropy. This preference is more prominent in the case of using W underlayer. This is because the film deposited on Ta layer contains more randomly aligned grains than that on W layer in terms of their XRD patterns shown in Fig.1. Figure 3(b) shows typical hysteresis loops for an isotropic film.

4 Discussion

It is known that a tetragonal unit cell tends to grow with its c-axis perpendicularly aligned if its lattice constant satisfies $c > a$, as it is easy to form perpendicular magnetocrystalline anisotropy in a $Nd_2Fe_{14}B$ film. When a crystallized buffer layer is employed, this tendency depends much on the epitaxial degree between the magnetic and the buffer layers. Here, the lattice mismatch parameter f is used to characterize the epitaxy, defined as

$$f = (a_0^{\rm u} - a_0^{\rm m})/a_0^{\rm m} = \Delta a_0/a_0^{\rm m}, \qquad (1)$$

where $a_0^{\rm m}$ and $a_0^{\rm u}$ refer to the unstrained lattice parameters of magnetic layer and underlayer, respectively. Because the M (M=Ta, Mo, or W) underlayer is (110) textured, f along the two directions of $(110)[003]||(00l)[100]$ and $(110)[2\bar{2}0]||(00l)[010]$ is calculated according to the XRD parameters of the corresponding bulk materials, respectively, as shown in Table 2. The results show that Mo and W layers should have better match with the $Nd_2Fe_{14}B$ $(00l)$ plane. According to Frank and van der Merwe's theory,[5] if the value of the mismatch parameter is less than ~9%, hetero-epitaxy could be formed between two layers. This is the case for W or even Ta underlayer. However, the actual experimental results are not always consistent with the theoretical predictions, as in the case of Mo underlayer. The cause of this is not known yet. But this phenomenon at least indicates that f is not the only parameter in determining the epitaxy. Other condition such as roughness or interlayer atomic diffusion may also play an important role. As shown in Fig.1, compared with the XRD patterns of other underlayers, the Mo (110) line is the most intense and narrowest, indicating that there exist the largest grains in the underlayer. Correspondingly, Mo underlayer has the roughest morphology. Too coarse surface may directly destroy the epitaxy of $Nd_2Fe_{14}B$ crystallites of $[00l]$ orientation on the Mo buffer layer.[6] Furthermore, no columnar grain structure could be developed on a coarse buffer layer. As a result, the tilted plate-like particles are produced, as shown in Fig.2. In addition, it has recently been found that the perpendicular magnetic anisotropy could be completely destroyed in the NdFeB films deposited on W underlayer at 420°C if a certain amount of Mo additive is doped into the magnetic layer. This indicates that a certain interaction between Mo atoms and the 2:14:1 structure may happen. Thus, the perpendicular alignment of c-axis is destroyed. The mechanism is under investigation. No strong hard magnetic properties are found in the 100nm thick NdFeB film deposited on Ta layer, and for a thickness of 300nm a high deposition temperature is needed to induce an evident perpendicular anisotropy,[4] compared with the case of deposition on W underlayer. This may be interpreted according to their different degrees of lattice mismatch with the $Nd_2Fe_{14}B$ $(00l)$ phase. But too high a temperature will also destroy the epitaxy growth of 2:14:1 crystallites due to the increasing irregular atomic diffusion agitated by the high atomic kinetic energy. This is the case of NdFeB films deposited on W layer at $T_{\rm s} > 490$°C.

Table 2. The calculated f along respective direction.

underlayer	$(110)[003]\|\|(00l)[100]$	$(110)[2\bar{2}0]\|\|(00l)[010]$
Ta	–12.6%	6.2%
Mo	–7.2%	1.1%
W	–7.8%	1.6%

The coercivity is an extrinsic property and directly depends on the microstructure, such as grain alignment, grain shape, defect, etc. This dependence can be qualitatively explained by a model for magnetization reversal developed by Kronmüller and Durst.[7] In this model, the coercivity for both pinning and nucleation reversal mechanisms is given by the following relation:

$$H_c = 2\alpha_{\rm K}\alpha_\varphi K_1/M_{\rm s} - N_{\rm eff}M_{\rm s}, \qquad (2)$$

where $\alpha_{\rm K}$ is the microstructural parameter on taking account of the reduction of the anisotropy at the inhomogeneities such as grain boundaries and crystal imperfections, and increases as the crystallization quality of hard magnetic grains is improved; α_ϕ is a mechanism-dependent parameter corresponding to the misalignment of grains and its value is 0.5 for a randomly aligned assembly of grains. $N_{\rm eff}$ is the local effective demagnetization factor much related to grain shapes. In Table 1, the coercivity increases with increasing $T_{\rm s}$. This can be attributed to the increase of the value of K_1 and $\alpha_{\rm K}$ due to the improvement of crystallization conditions. This is believed to be the main cause affecting the coercivities. The largest coercivity is obtained in the films without texture, e.g. deposited on Mo or W layer at high temperatures where the NdFeB film is isotropic. Seemingly, the coercivity is inversely proportional to the texture, which was also found by other authors.[6] In their discussions, this phenomenon was attributed to the better pinning of inverted domains in the interfacial regions across $Pr_2Fe_{14}B$ crystallites within a cluster, where the microstructure is crystallographically less aligned. But in our case, it is mainly assumed to be a smaller $N_{\rm eff}$ due to the nature of random alignment of the c-axis. In the textured NdFeB films, the biggest $N_{\rm eff}$ is 4π, e.g. at the surface regions or sharp corners or edges of hard magnetic grains. The reversed domains will nucleate at these local regions and quickly spread across most grains in the films. But the pinning of domain walls is inevitable at grain boundaries, or defect-like holes or nonmagnetic phase. This can be proven by the small tails of M–H loops in the third quadrant

shown in Figs.3 (a) and 3(c). In addition, although they are deposited at higher temperatures, textured NdFeB films on Ta layer show similar and even smaller coercivities than those films deposited on W underlayer at relatively low temperatures. This abnormality could be interpreted by the different values of α_ϕ. According to the micromagnetic simulation results, α_ϕ reduces if the average angle of grain misalignment increases but it is still smaller than 45°.[7] Since the textured NdFeB films deposited on W layer have better perpendicular orientation than that deposited on Ta layer, the former should have a higher α_ϕ value.

As a matter of fact, the maximum magnetic field is not enough to saturate some samples in this work, but the obtained coercivities are thought to be near the ideal values. Therefore, these results are useful in the comparison of the different influences of Ta, Mo, or W underlayer on the magnetic properties of the NdFeB films.

5. Conclusion

The microstructure of NdFeB films is closely related to the nature of underlayer materials and deposition temperature. Through adjusting the sputtering temperature, good perpendicular magnetic anisotropy could be produced in NdFeB films deposited on W or Ta underlayer. From the experimental results, it can be known that the mismatch parameter is not the only factor determining the film epitaxy, other consideration such as surface roughness or nonmagnetic elemental diffusion is also needed to be considered in order to acquire an epitaxial growth.

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