Effects of thickness and annealing condition on magnetic properties and thermal stabilities of Ta/Nd/NdFeB/Nd/Ta sandwiched films*

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Ta/Nd/NdFeB/Nd/Ta sandwiched films are deposited by magnetron sputtering on Si (100) substrates, and subsequently annealed in vacuum at different temperatures for different time. It is found that both the thickness of NdFeB and Nd layer and the annealing condition can affect the magnetic properties of Ta/Nd/NdFeB/Nd/Ta films. Interestingly, the thickness and annealing temperature show the relevant behaviors that can affect the magnetic properties of the film. The high coercivity of 24.1 kOe (1 Oe = 79.5775 A/m) and remanence ratio (remanent magnetization/saturation magnetization) of 0.94 can be obtained in a Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta film annealed for 3 min at 1023 K. In addition, the thermal stability of the film is also linked to the thickness of NdFeB and Nd layer and the annealing temperature as well. The excellent thermal stability can be achieved in a Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta film annealed at 1023 K.

Keywords: coercivity, thermal stability, thickness, annealing condition

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1. Introduction

NdFeB permanent magnetic films have received extensive attention due to their excellent hard magnetic properties and potential applications in micro-electromechanical system (MEMS), micro-magnetic devices, and magnetic recording media.[1–8] The relatively low coercivity and poor thermal stability of NdFeB commercial magnet are a practical obstacle for certain applications. The coercivity enhancement is one major focus to improve the properties of NdFeB film. Partial substitution of heavy rare earth element (Dy or Tb) for Nd has a significant effect on the coercivity enhancement, because $Dy_2Fe_{14}B$ or $Tb_2Fe_{14}B$ has a much higher anisotropy than $Nd_2Fe_{14}B$ phase.[9,10] However, due to the scarcity and high cost of Dy or Tb, it is necessary to develop high-coercivity Dy-free NdFeB films.

To increase the coercivity of NdFeB film, many researches have been done. $[NdFeB/Ta]_n$,[11] $[NdFeB/Nb]_n$,[12] $[NdFeB/NbCu]_n$,[13] $[NdFeB/FeMn]_n$[14] films each exhibit an improvement of permanent magnetic properties, of which the coercivities are respectively 11.6 kOe, 17.8 kOe, 19 kOe, and 17.2 kOe. Kim *et al.* reported that by annealing to diffuse the Nd element from Nd layer into NdFeB layer, the coercivity of Nd(0,1 μm)/NdFeB(0.3–1 μm)/Nd(0,1 μm) film increases abruptly to 20 kOe at $R = 1$ (R denotes the thickness ratio of Nd/NdFeB) and then keeps constant at 20 kOe at $R \geq 1$.[15] Li *et al.* reported that the coercivity fairly increases to 19.8 kOe because Nd elements effectively diffuse in $[NdFeB(650\ nm)/Nd]_4$ films annealed at 1073 K.[16]

In this work, Ta/Nd/NdFeB/Nd/Ta films are prepared on Si (100) substrates by magnetron sputtering. The high coercivity of 24.1 kOe and remanence ratio of 0.94 as well as excellent thermal stability are obtained in a Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta film annealed at 1023 K. It is also systematically investigated that the effects of the thickness of NdFeB and Nd layer and the annealing condition on the magnetic properties and thermal stabilities of Ta/Nd/NdFeB/Nd/Ta sandwiched films.

2. Experimental procedure

Nd/NdFeB/Nd films were prepared by the FJL560II ultra-high vacuum magnetron sputtering system on Si (100) substrates with a Ta underlayer of 60 nm and a Ta coverlayer of 60 nm, which were used to suppress the oxidation of NdFeB films. Pure Nd (99.9%) and Ta (99.95%) targets were used. The target for NdFeB layer is a commercial N33H NdFeB sintered target attached to B-chips. The base pressure of the deposition chamber was 2.0×10^{-4} Pa and high purity Ar gas was introduced during sputtering. The composition of NdFeB layer was determined to be $Nd_{10.73}Fe_{84.01}B_{5.26}$ by a Thermo System 7 energy dispersive spectrometer (EDS). The as-deposited films were subsequently annealed in vacuum at 873 K, 923 K, 973 K, 1023 K, and 1073 K, respectively.

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The structure of the films was analyzed by a Bruker-D8 x-ray diffraction (XRD) with Cu $K\alpha$ radiation. The thickness and morphology were characterized by a JSM-7001F field emission scanning electron microscope (FE-SEM). The magnetic properties were measured using a Quantum Design vibrating sample magnetometer (VSM) with a maximum applied field of 30 kOe.

3. Results and discussion

Figure 1 shows the XRD patterns of Ta/Nd(250 nm)/NdFeB (600 nm)/Nd(250 nm)/Ta and Ta/Nd(1000 nm)/NdFeB (600 nm)/Nd(1000 nm)/Ta films annealed for 30 min at 923 K and 1023 K. The tetragonal $Nd_2Fe_{14}B$ phase can be clearly identified by the prominent characterization peaks of (222), (114), (312), (410), and (116) in the XRD patterns. As annealing temperature increases, the relative intensities of (221), (114), and (116) peaks reduce, while the intensities of other $Nd_2Fe_{14}B$ peaks increase, suggesting that the alignment of the grains varies with the annealing temperature. Meanwhile, the $Nd_2Fe_{14}B$ peaks become sharper in Ta/Nd(1000 nm)/NdFeB(600 nm)/Nd(1000 nm)/Ta film than that in Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta film at the same annealing temperature, implying that the grains are growing. In addition to the above-mentioned peaks, Nd peaks are also observed in the XRD patterns, due to the Nd layer existing.

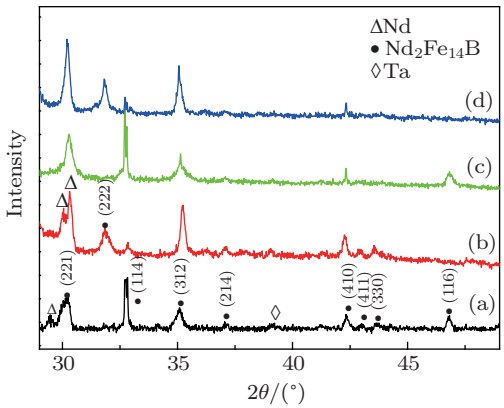


Fig. 1. (color online) XRD patterns of Ta/Nd(x nm)/NdFeB (600 nm)/Nd(x nm)/Ta films annealed for 30 min with (a) $x = 250$, at 923 K, (b) $x = 250$, at 1023 K, (c) $x = 1000$, at 923 K, (d) $x = 1000$, at 1023 K.

Figures 2(a) and 2(b) show the dependences of the in-plane and out-of-plane coercivities on NdFeB layer thickness in Ta/Nd(250 nm)/NdFeB/Nd(250 nm)/Ta films annealed for 30 min at different temperatures, respectively. On the one hand, both the in-plane and out-of-plane coercivities first increase and then decrease with the NdFeB layer thickness increasing. Interestingly, the maximum values of both in-plane and out-of-plane coercivities correspond to the different NdFeB layer thickness at different annealing temperatures. The highest coercivity of 23.2 kOe can be achieved at 600 nm NdFeB thickness, annealed at 1023 K. It can be explained by the strain energy arising, which is known to drive the crystallization of NdFeB as the NdFeB layer thickness and annealing temperature are suitable. It is hypothesized that the strain is minimized at the NdFeB layer of 600 nm annealed at 1023 K, which should be investigated in detail in the further study. On the other hand, when NdFeB layer thickness is less than 600 nm, both the in-plane and out-of-plane coercivities first increase as annealing temperature increases from 873 K to 1023 K, and then decrease as annealing temperature further increases to 1073 K. However, as NdFeB layer thickness is above 750 nm, both the in-plane and out-of-plane coercivities decrease monotonically with the annealing temperature increasing from 873 K to 1073 K. It may be interpreted that the grains grow with the increase of annealing temperature, resulting in the increase of coercivity. However, further increasing grain size may reduce the coercivity of the film.

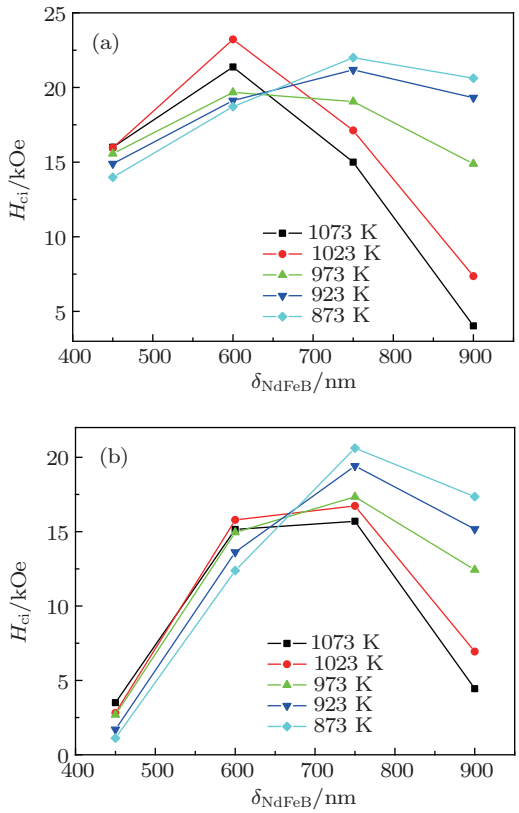


Fig. 2. (color online) Dependences of the (a) in-plane and (b) out-of-plane coercivities on NdFeB layer thickness in Ta/Nd(250 nm)/NdFeB/Nd(250 nm)/Ta films annealed for 30 min at different temperatures, respectively.

Figure 3(a) and 3(b) show the dependences of the in-plane and out-of-plane coercivities on Nd layer thickness in Ta/Nd/NdFeB(600 nm)/Nd/Ta films annealed for 30 min at different temperatures, respectively. With Nd layer thickness increasing, the in-plane coercivity almost increases monotonically, while the out-of-plane coercivity first increases and then

drastically decreases. At the same time, the in-plane coercivities first increase as annealing temperature increases from 873 K to 1023 K, and then decrease as annealing temperature further increasing to 1073 K. Also the out-of-plane coercivities show similar behaviors when Nd layer thickness is less than 500 nm. However, as Nd layer thickness increases to 750 nm, the out-of-plane coercivities decrease monotonically with the annealing temperature increasing from 873 K to 1073 K. It is believed that Nd atoms from Nd layer diffuse through the grain boundaries of the magnetic films, causing Nd-rich phase to form near the interface, which not only produces extra pinning sites for domain-wall movement but also reduces the interaction between the magnetic $Nd_2Fe_{14}B$ grains, resulting in an effective increase of the coercivity.[16,17] However, the thicker Nd layer may depress the *c*-axis texture, leading to the reduction of out-of-plane coercivity. In addition, the higher temperature, the more Nd atoms diffuse, so the out-of-plane coercivity decreases more rapidly for the films annealed at higher temperature with Nd layer increasing from 750 nm to 1000 nm, causing the out-of-plane coercivities to decrease with the increasing annealing temperature.

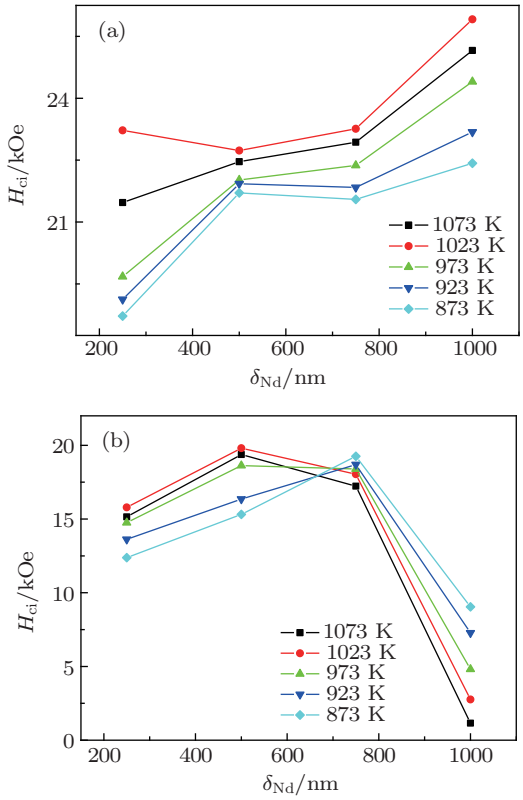


Fig. 3. (color online) Dependences of the (a) in-plane and (b) out-of-plane coercivities on Nd layer thickness in Ta/Nd/NdFeB(600 nm)/Nd/Ta films annealed for 30 min at different temperatures.

Figure 4 shows the cross-SEM micrograph of Ta/Nd(1000 nm)/NdFeB(600 nm)/Nd(1000 nm)/Ta film annealed at 1023 K. The boundary between Nd layer and NdFeB layer is not obvious, suggesting that the Nd atoms diffuse into the NdFeB layer. Meanwhile, the film shows a growth along the film plane with tiny spherical grains, which is in agreement with the above magnetization measurement.

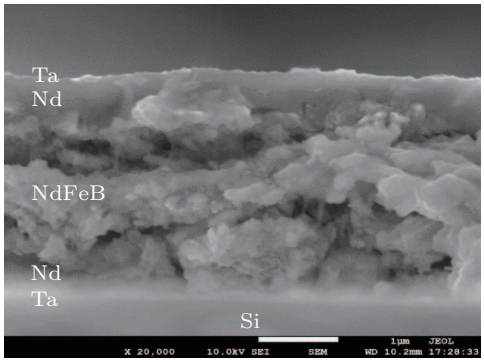


Fig. 4. Cross-SEM micrograph of Ta/Nd (1000 nm) / NdFeB (600 nm)/Nd(1000 nm)/Ta film annealed at 1023 K.

From the above discussion, it can be learned that if the suitable thickness of NdFeB and Nd layer and annealing temperature are chosen, the high coercivity can be achieved. Figure 5 shows the in-plane hysteresis loops of Ta/Nd(250 nm)/NdFeB(600 nm) /Nd(250 nm)/Ta film annealed for different time (3 min, 10 min, 30 min) at 1023 K. As seen in Fig. 5, the in-plane coercivity increases from 23.2 kOe to 24.1 kOe with the annealing time going from 30 min to 3 min. It can also be noticed that the remanence ratio reaches 0.94 in the film annealed for 3 min, which is also important for the application of NdFeB magnets. Surprisingly, the hysteresis loops show a kink near the original point due to the uncoupled soft magnetic grains existing. Moreover, with the annealing time decreasing, the kink becomes weaker. It can be induced that the grain grows with the increase of annealing time, resulting in that the grain annealed for 3 min is smaller than that annealed for 30 min, thereby increasing the coupled interaction between the magnetic grains.

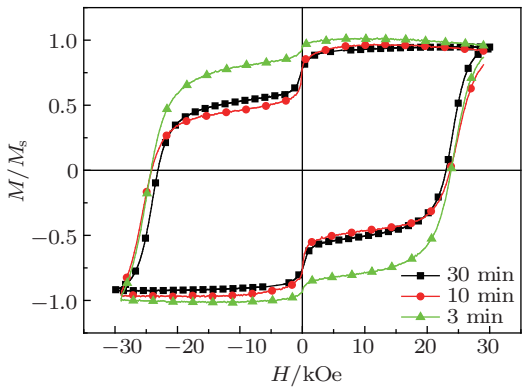


Fig. 5. (color online) Hysteresis loops of Ta/Nd(250 nm)/NdFeB (600 nm)/Nd(250 nm)/Ta films annealed at 1023 K.

Since high coercivity is obtained in Ta/Nd/NdFeB/Nd/Ta films, it is worth investigating the thermal stability of

coercivity at elevated temperature. Here we introduce a temperature coefficient of coercivity β to describe the thermal stability of coercivity, which is defined as $\beta = [H_{ci}(T) - H_{ci}(300)]/[H_{ci}(300) \times (T - 300)]$, with $H_{ci}(300)$ and $H_{ci}(T)$ representing the coercivity at 300 K (room temperature) and temperature T, respectively. Figure 6 shows the temperature dependences of the coercivities of Ta/Nd(250 nm)/NdFeB (t)/Nd(250 nm)/Ta (t = 600 nm, 900 nm) and Ta/Nd(750 nm)/NdFeB (600 nm)/Nd(750 nm)/Ta films annealed at 923 K as well as Ta/Nd(250 nm)/NdFeB(600 nm)/Nd (250 nm)/Ta film annealed at 1023 K. The coercivities of all the films decrease with temperature increasing. The β values (300 K–380 K) of the above films are shown in Table 1. It can be seen that the β values of all the films are different, indicating that the thermal stability of coercivity is related to the thickness of NdFeB and Nd layer, and annealing temperature as well. Furthermore, the β value of Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta film annealed at 1023 K is -0.469% K^{-1}, which is lower than the β value (from -0.5% K^{-1} to -0.6% K^{-1}) of commercial sintered magnets or hot pressed magnets.[18] This means that the film has excellent thermal stability than those of commercial magnets, thus suggesting that a magnetically isolated grain structure in Nd-diffusion processed film is beneficial to high temperature applications of NdFeB film.[19]

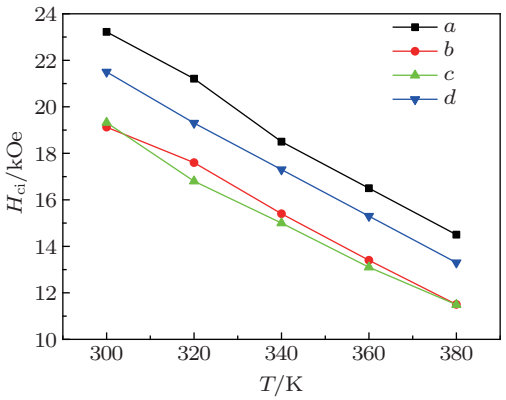


Fig. 6. (color online) Temperature dependences of the coercivities in Ta/Nd/NdFeB/Nd/Ta films: curve *a*, Ta/Nd(250 nm)/NdFeB (600 nm)/Nd(250 nm)/Ta annealed at 1023 K; curve *b*, Ta/Nd (250 nm) / NdFeB (600 nm)/Nd(250 nm)/Ta; curve *c*, Ta/Nd (250 nm)/NdFeB (900 nm) / Nd(250 nm)/Ta; and curve *d*, Ta/Nd(750 nm) / NdFeB(600 nm) / Nd(750 nm)/Ta. Here, the films of curves *b*–*d* are annealed at 923 K.

Table 1. β values (300 K–380 K) of Ta/Nd/NdFeB/Nd/Ta films.

Film	Annealing temperature/K	β value (300 K–380 K)
Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta	1023 K	-0.469% K^{-1}
Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta	923 K	-0.472 % K^{-1}
Ta/Nd(750 nm)/NdFeB(600 nm)/Nd(750 nm)/Ta	923 K	-0.476% K^{-1}
Ta/Nd(250 nm)/NdFeB(900 nm)/Nd(250 nm)/Ta	923 K	-0.508% K^{-1}

4. Conclusions

The magnetic properties and thermal stabilities of Ta/Nd/NdFeB/Nd/Ta films are strongly dependent on the thickness of NdFeB and Nd layer and the annealing condition. Moreover, the thickness and annealing temperature show the relevant behaviors that can affect the magnetic properties of the films. The high coercivity of 24.1 kOe and remanence ratio of 0.94 can be obtained in Ta/Nd(250 nm)/NdFeB(600 nm)/Nd(250 nm)/Ta film annealed at 1023 K. Meanwhile, the film has excellent thermal stability compared with commercial magnets. Altogether the results suggest that Ta/Nd/NdFeB/Nd/Ta film may have a significant potential application as the Dy-free permanent magnetic materials.

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