NdFe₁₂N_x hard-magnetic compound with high magnetization and anisotropy field

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The NdFe₁₂N_x compound with a ThMn₁₂ structure (space group I4/mmm) was successfully synthesized by nitriding the NdFe₁₂ layer that was grown on a W underlayer on a single crystalline MgO(001) substrate. The *c*-axis expanded from 0.480 to 0.492 nm while the *a*-axis showed a slight contraction from 0.852 to 0.849 nm after the nitriding. Excellent intrinsic hard magnetic properties of $\mu_0 M_s \sim 1.66 \pm 0.08$ T, $\mu_0 H_a \sim 8$ T, and $T_c \sim 550$ °C, which are superior to those of Nd₂Fe₁₄B, were obtained.

Keywords permanent magnet, hard magnet, ThMn₁₂ structure, Nd-Fe-N

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The development of a new high performance permanent magnet using less amount of rare earth elements receives intense research interest due to the world wide concern on the stable supply of strategic materials like (Nd,Dy)-Fe-B based permanent magnets¹. Anisotropic Nd-Fe-B magnets processed by a powder metallurgy route exhibit the highest maximum energy product, $(BH)_{\max}$, among all the permanent magnets.² The main phase of the Nd-Fe-B magnets is Nd₂Fe₁₄B, which has a saturation magnetization ($\mu_0 M_s$) of 1.6 T, anisotropy field ($\mu_0 H_a$) of about 7.5 T at room temperature^{3,4,5}, and a Curie temperature (T_c) of 313 °C.⁴ Because of the balanced magnetic hardness and saturation magnetization, there are no other permanent magnet materials that can challenge the Nd₂Fe₁₄B compound.

H_a is the theoretical limit of coercivity for coherent rotation, while the coercivities of industrially processed bulk magnets have never exceeded $H_a/3$. The theoretical limit of $(BH)_{\max}$ is described as $M_r^2/(4\mu_0)$ where M_r is the remanent magnetization. Since a certain fraction of a nonmagnetic phase (>10%) must be present in bulk magnets to introduce a heterogeneous microstructure to induce a coercive force, M_r is smaller than $0.9M_s$, where M_s is the saturation magnetization of a hard magnetic compound; hence, the upper limit for $(BH)_{\max}$ would be around $\mu_0(0.9M_s)^2/4$. Such $(BH)_{\max}$ can be obtained only when $H_c > M_r/2$; hence a hard magnetic compound that is suitable for permanent magnet application must have a sufficiently large anisotropy field, i.e., $H_c > H_a/3 > 0.9M_s/2$ or $H_a > 1.35M_s$. Therefore, finding a new hard

magnetic compound, whose M_s is higher than that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ with a sufficient magnetic hardness of $H_a > 1.35M_s$ is of great interest. During the past 32 years, no other compounds with intrinsic hard magnetic properties superior to $\text{Nd}_2\text{Fe}_{14}\text{B}$ have been found.

$R\text{Fe}_{12}$ (R : rare earth element) compounds are expected to have high magnetization since they have the highest content of Fe among R -Fe compounds in the R -Fe system. However, $R\text{Fe}_{12}$ compounds are unstable in the R -Fe binary systems. The $R\text{Fe}_{12}$ phase can only be obtained by replacing Fe with a third element M (M : Al, Cr, V, Ti, Mo, W, Si and Nb)^{6,7,8,9,10}, i.e., $R(\text{Fe}_{1-x}M_x)_{12}$. In these compounds, interstitial nitrogen dissolution is known to enhance T_c , M_s and H_a . The average increase of T_c by introducing nitrogen into the $R(\text{Fe},M)_{12}$ is about 200°C.¹¹ For example, T_c increases from 274 °C for $\text{NdFe}_{11}\text{Ti}$ to 467 °C for $\text{NdFe}_{11}\text{TiN}$,^{12,13} which is desirable for permanent magnet applications for high temperature operation such as the traction motors of electric vehicles. A slightly higher $\mu_0 H_a$ of 7.5 T and T_c of 600°C have been reported for the $\text{NdFe}_7\text{Co}_3\text{TiN}_{1.3}$ compound, in which a part of Fe in $\text{NdFe}_{11}\text{TiN}_x$ was substituted with Co.¹⁴ However, $\mu_0 M_s$ of 1.48 T for $\text{NdFe}_{11}\text{TiN}$ and of 1.50 T for $\text{NdFe}_7\text{Co}_3\text{TiN}_{1.3}$ are lower than that of $\text{Nd}_2\text{Fe}_{14}\text{B}$, which is due to the substitution of a non-magnetic element for Fe to stabilize the ThMn_{12} structure. Recently, Miyake *et al.* predicted that a higher magnetization could be achieved by the reduction of the M elements from the $\text{NdFe}_{12-x}M_x\text{N}$ using *ab initio* calculations.¹⁵ Hence, in this study, we explored the possibility of obtaining the $\text{NdFe}_{12}\text{N}_x$ phase

without the substitution of M for Fe to achieve a higher saturation magnetization while maintaining the magnetic hardness. We succeeded in growing epitaxial NdFe_{12} and $\text{NdFe}_{12}\text{N}_x$ films without any ternary element M on the W underlayer, and the intrinsic magnetic properties of the $\text{NdFe}_{12}\text{N}_x$ phase were found to be superior to those of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound.

NdFe_{12} films with thicknesses of about 70 nm and 360 nm were deposited on W-buffered single crystalline $\text{MgO}(100)$ substrates at 650°C by co-sputtering Nd and Fe targets. The 20 nm W-underlayer was deposited on the $\text{MgO}(001)$ substrate at 400°C . $\text{NdFe}_{12}\text{N}_x$ films were obtained by nitriding the NdFe_{12} films at 500°C for 1 h in the N_2 gas atmosphere of 2.0 Pa. The crystal structure and the lattice parameters were determined by x-ray diffraction (XRD) using a RIGAKU, SmartLab. SQUID-VSM (Quantum Design, Inc. MPMS SQUID VSM) was used to evaluate the magnetic properties in the temperature range of 300 to 950 K with a maximum magnetic field of 7 T. The microstructure was studied by transmission electron microscopy (TEM) using an aberration corrected scanning transmission electron microscope (STEM), FEI, TitanG2 80-200.

XRD patterns of NdFe_{12} and $\text{NdFe}_{12}\text{N}_x$ films with a thickness of about 70 nm are shown in Fig. 1. The peaks at around 37° and 75° are from the (002) and (004) diffractions of the NdFe_{12} and $\text{NdFe}_{12}\text{N}_x$ phases and the one at around 65° is from the (002) diffraction of the $\alpha\text{-Fe}$ phase in Fig. 1 (a). The (211), (031), (202), (222), (132), (332) and (323) peaks of $\text{NdFe}_{12}\text{N}_x$

were also detected by tuning the *chi* and *phi* angles as shown in Fig.1 (b). These peaks were shifted to lower angles after nitriding NdFe₁₂. The lattice parameters of the NdFe₁₂ and NdFe₁₂N_x phases were $a = 0.852$ nm, $c = 0.480$ nm and $a = 0.849$ nm, $c = 0.492$ nm, respectively. The a -axis showed a slight contraction and the c -axis had a volume expansion of about 2.0 % after nitriding. Although the Th₂Zn₁₇, TbCu₇ and ThMn₁₂ structures cannot be distinguished easily from the x-ray diffraction data due to their structural similarities,¹⁶ the identification of each structure can be made from their superlattice peaks. The superstructure reflections such as the (132) and (332) peaks in the ThMn₁₂ structure and the (015) and (024) peaks in the Th₂Zn₁₇ structure should be detectable. Although the (132) and (332) peaks of the ThMn₁₂ structure were measured before and after nitriding the samples as shown in Fig.1 (b), the (015) peak for Th₂Zn₁₇ at around 36° was not detected, which indicates that the main phase of these samples had the ThMn₁₂ structure. Both NdFe₁₂ and NdFe₁₂N_x films were grown with their c -axis perpendicular to the MgO(100) substrate.

Figure 2 shows the cross sectional STEM/EDS maps of the NdFe₁₂ and NdFe₁₂N_x films. The average thicknesses of the films calculated from the areas of the NdFe₁₂ and NdFe₁₂N_x layers were 69.2 ± 1 nm and 72.6 ± 1 nm, respectively. These layers contain a certain amount of the α -Fe phase as shown in the Fe map, the volume fractions of which were estimated from the area of the Fe-rich as indicated by the dashed lines in MAP. The calculated volume fractions of

α -Fe were about 11 % for the NdFe₁₂ film and 12 % for the NdFe₁₂N_x film. The volume fraction of α -Fe was estimated from an area five times larger than that shown in Fig. 2, which should provide sufficient statistical reliability for evaluating the volume fraction of α -Fe.

The hysteresis loops of the NdFe₁₂ and NdFe₁₂N_x films at room temperature are shown in Fig. 3. The anisotropy changed from in-plane to out-of-plane and H_a and M_s changed considerably after nitriding. The magnetic easy axis of NdFe₁₂N_x is parallel to the c -axis. The $\mu_0 H_a$ of NdFe₁₂N_x was estimated to be 8 T from the magnetic field where the extrapolated hard and easy axis magnetizations cross as shown in Fig.3 (b). The saturation magnetization of the magnetic layer was estimated to be 1.78 ± 0.02 T using the average thickness of the magnetic layer, 72.6 ± 1 nm, determined by TEM. The value of $\mu_0 M_s$ of the NdFe₁₂N_x phase, M_{NdFeN} , can be derived from this M_{measure} using $M_{\text{measure}} = xM_{\alpha\text{-Fe}} + (1-x)M_{\text{NdFeN}}$, where x is the volume fraction of α -Fe. The accuracy of M_{NdFeN} depends on the accuracy of x . The volume fraction of the α -Fe phase was estimated to be ~11% based on the EDS map in Fig. 3. Using this value, $\mu_0 M_s$ of NdFe₁₂N_x was deduced to be 1.72 T. The volume fraction of the soft α -Fe phase can also be estimated from the in-plane magnetization curve in Fig.3 (b). The initial magnetization rises at the low magnetic field is considered to be due to the magnetization of the soft-magnetic α -Fe phase. Based on the magnetization value that arises in the low magnetic field, the volume fraction of α -Fe was estimated to be about 30 %. Then, M_{NdFeN} , was deduced to be 1.66 ± 0.08 T.

The error was estimated from the difference in the volume fraction of the α -Fe phase estimated by the STEM-EDS map and the magnetization curve.

Figure 4 shows the temperature dependence of $\mu_0 H_a$ and $\mu_0 M_s$ of the $\text{NdFe}_{12}\text{N}_x$ phase. The values for $\text{Nd}_2\text{Fe}_{14}\text{B}$ taken from Ref. 17 are also plotted in the same figure for comparison. $\mu_0 H_a$ decreases lineally as a function temperature, which is slightly higher than that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ throughout the temperature range (Fig.4 (a)). T_c was estimated to be $\sim 550^\circ\text{C}$ by extrapolating the temperature dependence of the magnetization. The M - T curve in Fig. 4 (b) shows that $\text{NdFe}_{12}\text{N}_x$ starts to decompose at around 570°C and then the magnetization becomes higher due to the resultant formation of α -Fe. These figures show that $\mu_0 M_s$, $\mu_0 H_a$, and T_c of the $\text{NdFe}_{12}\text{N}_x$ phase are all higher than those of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

Although the intrinsic magnetic properties of the $\text{NdFe}_{12}\text{N}_x$ film are superior to those of $\text{Nd}_2\text{Fe}_{14}\text{B}$, a question is whether or not the phase can be stable in bulk. In this work, we stabilized the NdFe_{12} phase by using a W underlayer that has a good lattice matching with the NdFe_{12} phase and where the Fe and Nd do not diffuse into the W underlayer. The lattice misfit with the NdFe_{12} ($a = 0.852$ nm) was calculated to be 4.3 % with respect to $1/2\sqrt{2}a$ for W (0.3156 nm, bcc structure) since $\text{NdFe}_{12}\langle 001 \rangle$ was parallel to $\text{W}\langle 110 \rangle$. This good lattice matching stabilized the NdFe_{12} phase on the W underlayer even in the absence of the M element. We have also explored other underlayers such as V and Mo that showed a better lattice

mismatch with NdFe_{12} ; however, among the underlayers only the W underlayer led to the formation of the NdFe_{12} phase. Fe diffused into the V and Mo layers at 650°C . We confirmed that the $\text{NdFe}_{12}\text{N}_x$ layer can be grown at least up to 360 nm in thickness, indicating that once a thin layer of the ThMn_{12} phase is inoculated on the W underlayer, the ThMn_{12} phase can continue to grow even without ternary *M* elements. This suggests that the synthesis of $\text{NdFe}_{12}\text{N}_x$ powder could be possible if an appropriate processing condition is found. However, the decomposition temperature of 570°C is nearly equal to that for $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, suggesting that the densification by the conventional high temperature sintering process is not possible. Hence, an appropriate powder synthesis method and a low temperature densification process are both necessary for developing $\text{NdFe}_{12}\text{N}_x$ based bulk permanent magnets.

In conclusion, epitaxial NdFe_{12} films were prepared on a W buffered $\text{MgO}(100)$ substrate by using the co-sputtering process. By nitriding the NdFe_{12} film, the $\text{NdFe}_{12}\text{N}_x$ film was synthesized with intrinsic hard magnetic properties superior to those of $\text{Nd}_2\text{Fe}_{14}\text{B}$, i.e., $\mu_0 M_s \sim 1.66 \pm 0.08$ T, $\mu_0 H_a \sim 8$ T and $T_c \sim 550^\circ\text{C}$. The phase was shown to be stable with a 360 nm thickness, which indicates that there is a possibility to prepare bulk $\text{NdFe}_{12}\text{N}_x$ without the replacement of Fe with ternary structure stabilizing elements. Considering the intrinsic hard magnetic properties superior to those of $\text{Nd}_2\text{Fe}_{14}\text{B}$ satisfying the condition of $H_a >> 1.35 M_s$ with a lower Nd content with respect to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, the $\text{NdFe}_{12}\text{N}_x$ phase is a new promising

hard magnetic compound for high performance permanent magnets.

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Figure Captions

Fig.1 XRD profiles for (a) NdFe and NdFe₁₂N_x films when $\chi = 0$ and (b) NdFe₁₂N_x when χ and ϕ were tuned to detect signal from the (211), (031), (202), (222), (132), (332) and (323) peaks.

Fig.2 (Color online) STEM/EDX image of (a) NdFe₁₂ and (b) NdFe₁₂N_x with an average thickness of 69.2 ± 1 nm and 72.6 ± 1 nm, respectively. The area surrounded by the dashed line in the MAP corresponds to the α -Fe phase.

Fig.3 (Color online) hysteresis loops of (a)NdFe₁₂ and (b)NdFe₁₂N_x with a small amount of α -Fe.

Fig.4 (Color online) (a) Anisotropy field $\mu_0 H_a$ and (b) Saturation magnetization $\mu_0 M_S$ as a function of temperature along with those of Nd₂Fe₁₄B.¹⁷

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Figure 1

Figure 2

Figure 3

Figure 4