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## N site ordering effect on partially ordered Fe<sub>16</sub>N<sub>2</sub>

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Partially ordered Fe<sub>16</sub>N<sub>2</sub> thin films have been fabricated on Fe (001)-buffered GaAs (001) single-crystal substrates by a facing target sputtering process. The saturation magnetization has been systematically investigated as a function of N site ordering in partially ordered Fe<sub>16</sub>N<sub>2</sub> thin films, which is found to be increased monotonically with the increase in the N site ordering parameter, reaching up to 2.68 T at high ordering case. A model discussion is provided based on the partial localization of 3*d* electron states in this material system, which successfully rationalizes the formation of the giant saturation magnetization in chemically ordered Fe<sub>16</sub>N<sub>2</sub>. We further demonstrate that the average magnetic moment of partially ordered Fe<sub>16</sub>N<sub>2</sub> sensitively depends on the special arrangement of Fe<sub>6</sub>N clusters, which is the key to realize high magnetic moment in this material system. © 2011 American Institute of Physics. [doi:10.1063/1.3560051]

In the interstitial Fe–N compounds, when the Fe/N atomic ratio approaches  $\sim 8/1$ , upon proper tempering, the martensite phase  $\alpha'$ -Fe<sub>8</sub>N with randomly distributed N transforms into a chemically ordered  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> phase. In the magnetic research community, the magnetism of Fe<sub>16</sub>N<sub>2</sub> has been a mystery for 40 years due to the inconsistent experimental reports on its saturation magnetization ( $M_s$ ).<sup>1–8</sup> Experimentally, one of the biggest issues in regard to measuring its  $M_s$  is the challenge to produce a pure-phase sample. In most reports, the obtained Fe<sub>16</sub>N<sub>2</sub> phase is “partially ordered” in the sense that only part of the N atoms occupy the ordered sites. In particular, an Hitachi research group<sup>2</sup> produced N highly ordered single crystal Fe<sub>16</sub>N<sub>2</sub> using the molecular beam epitaxy method, and obtained a giant  $M_s$  that ranged from 2.8–3.0 T. On the other hand, similar epitaxial Fe–N films have been fabricated by research groups using other techniques such as dc sputtering,<sup>3,5,7</sup> facing target sputtering,<sup>4</sup> sputtering beam,<sup>6</sup> and ion beam.<sup>8</sup> The  $M_s$  evaluated for these films was significantly reduced. This is arguably interpreted as being caused by the presence of the N disordered phase with nonhigh  $M_s$ . However, the magnetism of both disordered Fe<sub>8</sub>N and ordered Fe<sub>16</sub>N<sub>2</sub>, especially the correlation between the magnetic moment and the degree of N site ordering is still missing.

In this letter, we report the synthesis and characterization of N partially ordered Fe<sub>16</sub>N<sub>2</sub> thin films, systematically studying their magnetic properties as a function of the N site ordering (*D*). It is found that as *D* increases, the  $M_s$  of the Fe–N layer increases monotonically. As the ordering parameter exceeds 0.3, the  $M_s$  of the Fe–N layer can reach an average value of 2.6 T, with the highest  $M_s$  of  $\sim 2.68$  T. For the disordered and low ordering samples, the measured  $M_s$  values range from 2.0–2.3 T. In a previous study,<sup>9</sup> we proposed an “atom (Fe)+cluster (Fe<sub>6</sub>N)” model to rationalize the formation of giant magnetization in a well-ordered Fe<sub>16</sub>N<sub>2</sub> crystal. Here we further show that for the partially

ordered case, the magnetization of this material system sensitively depends on the spatial arrangement of these Fe<sub>6</sub>N clusters, which allows the system to evolve from behave nonhigh  $M_s$  to giant  $M_s$  upon long range chemical order.

Thin films of partially ordered Fe<sub>16</sub>N<sub>2</sub> were grown on Fe(001) buffered (001)-oriented GaAs single crystal substrates by using a facing target sputtering method. *In situ* postanneal the samples at 120 °C introduces different degree of N site ordering as discussed below in detail. The phase structure are characterized by a Siemens D5005 x-ray diffractometer with Cu *K* $\alpha$  radiation and scanning transmission electron microscopy (JEOL 2200FS). The magnetic properties of the films were examined by vibrating sample magnetometry (Princeton Measurements). The hysteresis (M-H) loops were measured by applying a magnetic field up to 10 kOe in the film plane at room temperature. Uncertainty in the film volume determination is  $\sim 3\%$ , as the film thickness was determined by XRR and cross-checked by TEM. The absolute value of magnetization typically falls in the range of  $10^{-3}$ – $10^{-4}$  emu with alignment error of  $\sim 3\%$ .

Figure 1(a) shows the x-ray diffraction (XRD) pattern of the prepared Fe–N samples, a common peak at 58.8° is observed, corresponding to diffraction from the Fe<sub>16</sub>N<sub>2</sub>(004) and Fe<sub>8</sub>N(002) planes. The Fe<sub>16</sub>N<sub>2</sub>(002) peak at  $\sim 28.6^\circ$  develops after *in situ* postannealing for different annealing times. As the degree of N ordering increases, the Fe<sub>16</sub>N<sub>2</sub>(002) peak becomes prominent. By comparing the integrated intensity ratio of  $I^{\text{obs}}(002)/I^{\text{obs}}(004)$ , the degree of N site ordering<sup>6</sup> can be quantitatively investigated using what is defined as

$$D = \frac{I^{\text{obs}}(002)/I^{\text{obs}}(004)}{I^{\text{cal}}(002)/I^{\text{cal}}(004)},$$

where  $I^{\text{obs}}(002)$  and  $I^{\text{obs}}(004)$  denote the integrated intensity of peaks according to the measurement.  $I^{\text{cal}}(002)$  and  $I^{\text{cal}}(004)$  represent integrated intensity these two peaks calculated from ordered Fe<sub>16</sub>N<sub>2</sub>.

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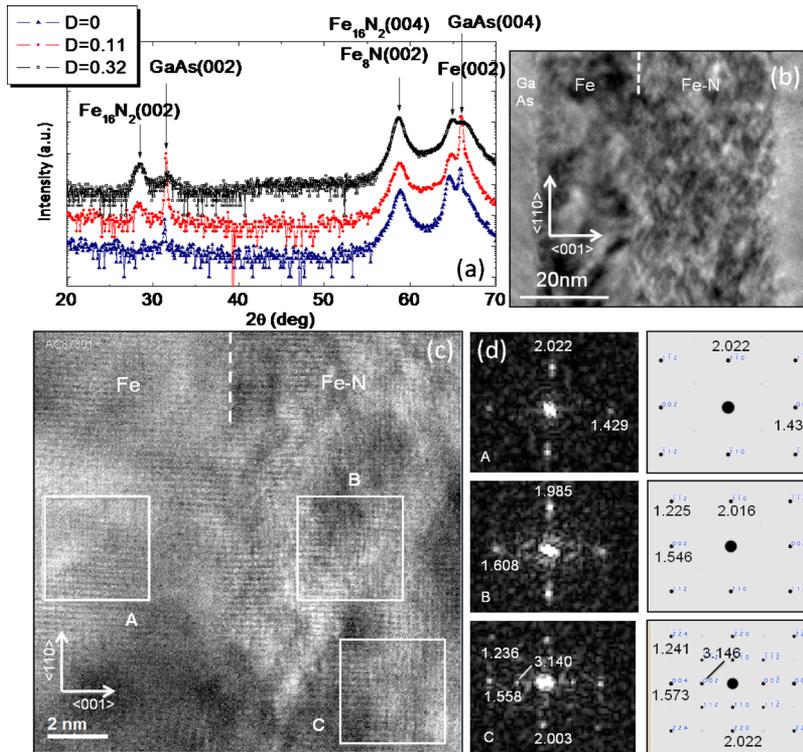


FIG. 1. (Color online) (a) XRD of partially ordered  $\text{Fe}_{16}\text{N}_2$  samples with different N ordering parameter ( $D$ ) as calculated. (b) Cross-section TEM image of partially ordering Fe-N sample with layer structure Fe-N/(Fe/GaAs). (c) High resolution BF-STEM lattice image of the Fe-N layer showing Fe{110} zone axis. (d) Computed diffractograms with associated periodicities identified, from the respective areas A–C shown in (c), along with the computed diffraction patterns for area A:  $\alpha$ -Fe, area B: Fe-N martensite, and area C:  $\text{Fe}_{16}\text{N}_2$  (see text for details).

The  $D$  values are therefore calculated from the above equation for these three typical samples, which can range from 0 to above 0.3. Figure 1(b) shows a bright-field scanning-transmission electron image (BF-STEM) of the cross section of one partially ordered sample ( $D=0.32$ ). A zoom-in look at Fe/Fe-N interface is acquired from an Aberration-corrected high-angle annular BF image, which [Fig. 1(c)] shows the epitaxy of the lattice structure of the Fe-N layer and is coherent with the  $\alpha$ -Fe buffer. To analyze the periodicities in Fig. 1(c), diffractograms from outlined regions A, B, and C were computed, which closely matched the known  $d$ -spacings for the  $\alpha$ -Fe, Fe-N martensite, and  $\text{Fe}_{16}\text{N}_2$  with  $\langle 110 \rangle$  zone axis, respectively, as shown in Fig. 1(d).

Figure 2(a) shows the M-H loops of partially ordered sample with  $D=0.34$ . M-H loop for the Fe-only sample is also plotted for comparison. It is seen the pure Fe (22 nm) sample gives an  $M_s$  of 2.02 T after averaging multiple measurements. However, after Fe-N layer grown on top, the entire sample produces an  $M_s$  up to 25% larger than that of Fe-only sample, which is significantly larger than the testing error bar for our measurement system (VSM+XRR  $\sim 6\%$ ), suggesting the presence of a much higher  $M_s$  value in the Fe-N layer. Figure 2(b) plots the  $M_s$  values of the Fe-N layer as a function of Fe-N layer thickness for the partially ordered  $\text{Fe}_{16}\text{N}_2$  samples at different  $D$ . From the figure the  $M_s$  of the disordered  $\text{Fe}_8\text{N}$  ( $D=0$ ) is determined to be  $\sim 2.04 \pm 0.12$  T at different thicknesses, which is very close to the  $M_s$  value obtained on pure Fe. As the degree of N site ordering increases, a systematic increment of  $M_s$  is present. In addition, a clear correlation between the degree of N site ordering and the average  $M_s$  of the Fe-N layer is seen at a fixed film thickness structure as shown in Fig. 2(c). The  $M_s$  increases monotonically as the degree of N ordering increases. At  $D > 0.3$ , the average  $M_s$  is evaluated to be about

2.6 T. The sample with the highest saturation magnetization of  $\sim 2.68$  T of Fe-N layer was obtained.

In general, the magnetism of  $3d$  transition metals is governed by the Slater-Pauling curve, where a magnetic moment of  $2.5 \mu_B$  per atom is considered as the upper limit. This is far below the experimental claim ( $3.2 \mu_B/\text{Fe}$ ) observed on the single-phase  $\text{Fe}_{16}\text{N}_2$  samples,<sup>2</sup> sputtering beam prepared epitaxial samples ( $2.9 \mu_B/\text{Fe}$ ) (Ref. 6) as well as the present results ( $2.93 \mu_B/\text{Fe}$ ). It is also seen that in all these experiments, the degree of N site ordering strongly affects the average magnetic moment of the Fe/N=8/1 ( $\alpha' + \alpha''$ ) system. In our previous study,<sup>9</sup> a “cluster+atom” model was proposed, which predicts the existence of high magnetization in  $\text{Fe}_{16}\text{N}_2$ . In particular, the N atom occupies every other octahedron; therefore no neighboring clusters are shared by a common iron atom site [Fig. 3(a)]. In particular as shown on Fig. 3(a) strong Coulomb interaction is brought up due to the charge difference interior and exterior to the cluster region, and consequently leads to the appearance of localized electrons on Fe sites within the Fe-N clusters (Fe 4e and Fe 8h), and itinerant bandlike electrons on the rest of the Fe sites (Fe 4d) outside the clusters. To estimate its average magnetic moment, for highly localized electrons residing on Fe 4e and Fe 8h sites, a  $4 \mu_B/\text{Fe}$  is expected given Hund’s first rule in the atomic limit. On the other hand, if a moment of  $2.0 \mu_B/\text{Fe}$  for the itinerant electrons is considered on the Fe 4d, an average magnetic moment of  $\sim 3.5 \mu_B/\text{Fe}$  is obtained on the chemically ordered  $\text{Fe}_{16}\text{N}_2$ . However, in  $\text{Fe}_8\text{N}$ , due to the N random occupation, there exists both N-rich and N-poor local regions, as schematically shown in Figs. 3(b) and 3(c). In the N-rich case, the redundancy of Fe-N clusters inevitably causes the appearance of “connected” neighboring Fe-N clusters, in which the corner-shared or edge-shared Fe atoms are present. These Fe atoms closely resemble the local chemical environment of Fe sites in N-rich phases such as  $\text{Fe}_4\text{N}$  or  $\text{Fe}_3\text{N}$ ; in which case, the

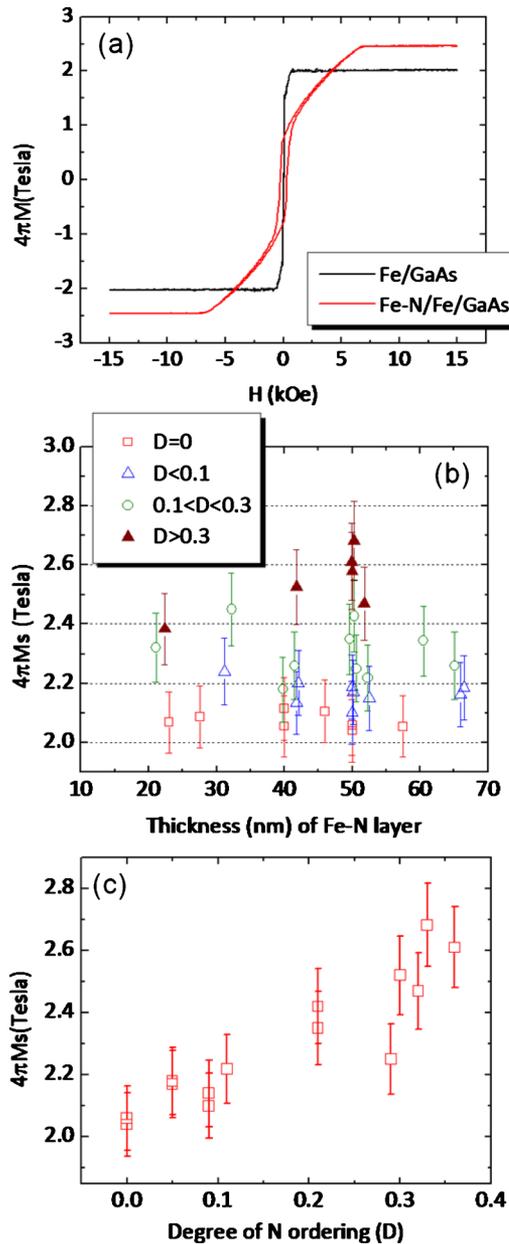


FIG. 2. (Color online) (a) In-plane M-H loops of Fe(24 nm)/GaAs (black) and partially ordered ( $D=0.34$ )  $\text{Fe}_{16}\text{N}_2$ (50 nm)/Fe(24 nm)/GaAs; (b) thickness dependence of  $M_s$  for partially ordered  $\text{Fe}_{16}\text{N}_2$  films at different degree of N site ordering ( $D$ ); and (c)  $M_s$  as a function of  $D$  for samples with calibrated structure of Fe-N(50 nm)/Fe(24 nm)/GaAs.

significant charge difference brought up in a “separated cluster” scenario disappears. Consequently, electrons residing on these sites evolve from highly localized atomiclike states to itinerant bandlike states, again due to the reduction in Coulomb interaction. In the N-poor case, though the “cluster separation” is still maintained, the dominant population of Fe sites is metalliclike, which also leads to the reduction in average magnetic moment. To give a quantitative estimation, in  $\alpha'$ - $\text{Fe}_{16}\text{N}_2$ , 75% of iron sites (Fe 4e and Fe 8h) have only one N as the nearest neighbor (NN). The remaining 25% consists only of Fe 4d with no surrounding N. However, in  $\alpha'$ - $\text{Fe}_8\text{N}$ , the percentage of iron sites with 0, 1, 2, and 3 N atom(s) as NN was calculated under the binomial distribu-

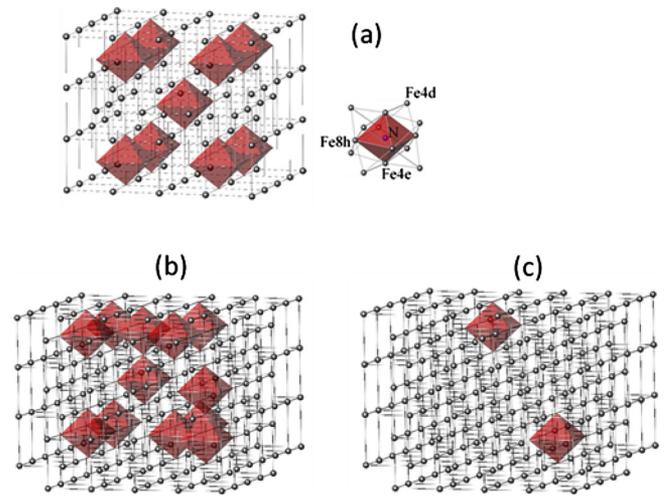


FIG. 3. (Color online) (a)  $\text{Fe}_{16}\text{N}_2$  crystal structure; (b) N rich local region in  $\text{Fe}_8\text{N}$ ; and (c) N poor local region in  $\text{Fe}_8\text{N}$ .

tion assumption using the following equation. The result is summarized below

| $m$       | 0     | 1     | 2     | 3    | Total |
|-----------|-------|-------|-------|------|-------|
| $P_m$ (%) | 44.88 | 38.47 | 13.74 | 2.61 | 0.997 |

where  $P_m$  is defined as the percentage of the iron sites that have  $m$  N atoms as NN. Similarly, we consider that highly localized Fe sites ( $m=1$  case) possess a magnetic moment of  $4 \mu_B$  and bandlike Fe sites ( $m=0, 2$ , and  $3$ ) possess a moment of  $2 \mu_B$ . The average magnetic moment of  $2.6 \mu_B/\text{Fe}$  is obtained, which is substantially lower than that of  $\text{Fe}_{16}\text{N}_2$ . Furthermore, in a view consistent with bond percolation theory, the threshold impurity concentration  $P_c$  is 0.12 for an fcc lattice,<sup>10</sup> which is less than that in Fe/N=8/1 case ( $p=0.125$ ). This suggests a random distribution of the N in this lattice system would cause a global connection of Fe-N octahedral clusters and give rise to bandlike iron behavior, in which case all the localized Fe states will disappear and further reduces the average magnetic moment.

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