Growth of ferromagnetic Fe_4N epitaxial layers and *a*-axis-oriented Fe_4N/MgO/Fe magnetic tunnel junction on MgO(001) substrates using molecular beam epitaxy

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Abstract

a-axis-oriented 80-nm-thick γ'-Fe_4N films were epitaxially grown on MgO(001) substrates by supplying the Fe and N sources on the pre-deposited *a*-axis-oriented 30-nm-thick α-Fe epitaxial film. This technique has been used to form highly *a*-axis-oriented Fe_4N(75 nm)/MgO(1 nm)/Fe(100 nm) magnetic tunnel junctions (MTJ)s from the Fe(7 nm)/MgO(1 nm)/Fe(100 nm) on the MgO(001) substrate. Magnetization versus the magnetic field curve of the MTJ was measured at 280 K, and a two-step hysteresis loop was clearly observed. This observation shows that the two ferromagnetic layers were separated by a 1-nm-thick MgO barrier.

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1. Introduction

Spintronics, an emerging area in electronics, which is based on the combination of magnetic and semiconducting materials, has attracted significant attention in recent years. The tunnel magnetoresistance (TMR) effect in magnetic tunnel junctions (MTJs), which consists of two ferromagnetic layers separated by an insulating layer, has also been extensively studied [1, 2]. One way to realize a large TMR ratio is to grow a MTJ using a crystalline barrier, in which coherent electron tunneling without spin scattering may be expected [3, 4]. Another way involves the use of highly spin-polarized ferromagnetic materials such as electrodes [5, 6]. Thus, numerous different types of half metals and hetero junctions have been studied extensively.

Iron nitrides have attracted significant attention as spintronic materials. These materials have unique features including high-hardness, chemical inertness, and high electrical conductivity. Among them, ferromagnetic α”-$Fe_{16}N_2$, γ’-Fe_4N and ε-$Fe_{2\text{-}3}N$ have been extensively studied for applications in high-density magnetic recording heads and media [7-17]. We have succeeded in the epitaxial growth of ε-Fe_3N on Si(111) [18], as well as the formation of highly-oriented nitride-based crystalline Fe_3N/AlN/Fe_4N MTJs by molecular beam epitaxy (MBE) using iron-pentacarbonyl ($Fe(CO)_5$) as an Fe source and nitrogen radical beams produced by electron cyclotron resonance (ECR) plasma [19]. Kokado *et al*. theoretically predicted highly spin-polarized transport in γ’-Fe_4N, therefore, this iron nitride

has attracted significant attention [20]. Recently, an inverse TMR effect was reported in Fe_4N/MgO/CoFeB MTJ that was fabricated by sputtering [21]. However, high-spin polarization has not yet been reported for γ'-Fe_4N. Therefore, we expect that γ'-Fe_4N films are a good candidate. The epitaxial growth of γ'-Fe_4N films has been reported by various growth techniques including; reactive sputtering in ambient NH_3 [10], ion-beam assisted evaporation [11], MBE of iron in the presence of an atomic nitrogen produced by radio-frequency plasma [12, 13], halide vapor phase epitaxy using $Fe(Cl)_3$ and NH_3 [14]. However, there have only been a limited number of papers on the epitaxial growth of γ'-Fe_4N films [12-14]. Furthermore, there have been no reports on the growth of Fe_4N/MgO/Fe_4N MTJs.

Herein, we report the epitaxial growth of γ'-Fe_4N films by a simple method, that is, by nitriding the predeposited *a*-axis-oriented α-Fe epitaxial layers on MgO(001) using ECR-N_2 and $Fe(CO)_5$. The highly *a*-axis-oriented Fe_4N/MgO/Fe MTJ was also formed using this technique. The probable method of formation of Fe_4N/MgO/Fe_4N MTJ and the magnetic properties of the γ'-Fe_4N films as well as the MTJ are discussed.

2. Experimental procedures

γ'-Fe_4N films and Fe_4N/MgO/Fe MTJ were prepared by MBE using $Fe(CO)_5$ as a Fe source and a nitrogen radical beam produced by ECR plasma as follows. In the case of γ'-Fe_4N films, first, *a*-axis-oriented 30-nm-thick α-Fe layers were epitaxially grown at 450 ºC

using $Fe(CO)_5$ on an MgO(001) substrate after cleaning the substrate at 900 ºC for 60 min in an ultra high vacuum. Then, the $Fe(CO)_5$ and ECR-N_2 were supplied simultaneously at 450 ºC on the α-Fe layers. During growth, the α-Fe layers were nitrided to form γ'-Fe_4N. As a control, a sample formed by supplying the Fe and N sources on a thinner α-Fe layer (7 nm) was prepared. In addition, a sample formed by supplying only the N source was prepared. In the case of γ'-Fe_4N MTJ, the $Fe(CO)_5$ and ECR-N_2 were supplied simultaneously at 450 ºC on the *a*-axis-oriented Fe(7 nm)/MgO(1 nm)/Fe(100 nm)/MgO structure. During growth, the upper α-Fe layers were nitrided to form the γ'-Fe_4N and a 75-nm-Fe_4N film was grown. The crystallinity of the grown layers was characterized by θ-2θ X-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED). All the RHEED patterns were taken from the [100] azimuth of MgO. A superconducting quantum interference device (SQUID) magnetometer was used to measure the magnetic properties of the samples.

3. Results and discussion

Figure 1(a) shows the θ-2θ XRD pattern of the 30-nm-thick α-Fe layers on MgO(001). Together with the inserted RHEED pattern, the *a*-axis-oriented α-Fe film was epitaxially grown. Since the lattice constant of MgO (0.421 nm) is almost the same as that of α-Fe (0.287 nm) multiplied by $\sqrt{2}$, the *a*-axis-oriented α-Fe is rotated by 45º on MgO(001) as shown in Fig. 2(a), that is; α-Fe(100)//MgO(001) with α-Fe[010] or [001]//MgO[110].

Figures 1(b)-1(e) are the θ-2θ XRD patterns of the samples obtained after 8, 15, 25 and 30 min. The peak intensity of α-Fe(200) decreased gradually with increasing the growth duration, and almost disappeared after 30 min. In contrast, the peak intensity of γ'-Fe_4N(200) increased and the thickness of γ'-Fe_4N became approximately 80 nm after 30 min, suggesting that the *a*-axis-oriented α-Fe layer was nitrided to become *a*-axis-oriented γ'-Fe_4N. The diffraction peak of α-Fe(200) disappeared completely after 60 min in the case of the thinner α-Fe layer (7 nm), as shown in Fig. 1(f). The spotty RHEED pattern of γ'-Fe_4N shown in Fig. 1(e) suggests that the epitaxial orientation of γ'-Fe_4N on MgO(001) can be explained by Fig. 2(b); that is Fe_4N(100)//MgO(001) with Fe_4N[010] or [001]//MgO[100]. It is important to note that after several minutes, as shown in Figs. 1(b) and 1(c), the diffraction peak of γ'-Fe_4N emerged. In addition, the diffraction peak of γ'-Fe_4N was too weak to be seen as shown in Fig. 1(g), when only the N source was supplied to the Fe/MgO. These results indicate that the transformation of the predeposited α-Fe layers into γ'-Fe_4N occurs gradually in the surface region of the α-Fe. This layer is then likely to work as a template for the overlayers, directing the reaction of Fe and N sources to form γ'-Fe_4N layers. This results in the sudden increase in XRD intensity of γ'-Fe_4N, as shown in Fig.1(c).

Figure 3 shows the magnetization versus magnetic field (*M-H*) curve measured for the Fe_4N(80 nm)/MgO sample at 280 K. The external *H* was applied parallel to the sample surface. The coercive field, H_c, is approximately 250 Oe. The saturation magnetization, M_s,

was deduced from the *M-H* curve to be approximately 1470 emu/cm^3. This value is in good agreement with that of bulk γ'-Fe_4N [22]. Spin polarization of the γ'-Fe_4N epitaxial layers is now under evaluation by Andreev reflection measurements.

Figures 4(a) and 4(b) show the θ-2θ XRD patterns of samples obtained (a) before growth (MgO(1 nm)/Fe(100 nm)/MgO(001) sub.) and (b) after 60 min of simultaneous supply of Fe and N sources to the *a*-axis-oriented α-Fe(7 nm) layer on the MgO/Fe/MgO. The diffraction peaks of α-Fe(200) and γ'-Fe_4N(200) were clearly observed in Fig. 4(b), showing that the *a*-axis-oriented MTJ was formed. The results shown in Fig. 1, indicate that the 7-nm-thick α-Fe layer was entirely transformed into γ'-Fe_4N layers. Furthermore, the peak intensity of α-Fe(200) in Fig. 4(b) became approximately half of that of Fig. 4(a). Thus, we speculate that the upper region of the Fe layer on the bottom was likely to transform into γ'-Fe_4N, indicating probable formation of Fe_4N/MgO/Fe_4N MTJ. Previously, we reported the formation of Fe_3N/AlN(2 nm)/Fe_4N MTJ when the same Fe and N sources were supplied to form ε-Fe_3N layers on the AlN(2 nm)/Fe(30 nm) structure [19]. Rutherford backscattering spectroscopy measurements revealed that the Fe layer was nitrided to form γ'-Fe_4N through the 2-nm-thick AlN barrier layer during growth of the ε-Fe_3N layers. We speculate that a similar event may occur in the current work.

Figure 5 shows the *M-H* curve measured for the MTJ at 280 K. The external *H* was applied parallel to the sample surface. A clear two-step hysteresis loop can be observed, which

is typical for MTJs. This may be attributed to the difference in H_c between the top and bottom ferromagnetic layers, showing successful formation of the two ferromagnetic layers separated by the MgO barrier layer. The M_s values were well explained by the bulk γ'-Fe_4N and α-Fe. The H_c values are 200 and 40 Oe, and originate from the top γ'-Fe_4N and the bottom α-Fe layers, respectively. However, the possible formation of very thin layers of γ'-Fe_4N between the MgO barrier layer and the bottom α-Fe layer cannot be ruled out. Therefore, further studies are necessary in order to determine what actually occurs in the bottom α-Fe layer.

4. Conclusions

a-axis-oriented 80-nm-thick γ'-Fe_4N epitaxial layers were grown on MgO(001) substrates by MBE using $Fe(CO)_5$ as a Fe source and ECR-N_2 as an N source. When the Fe and N sources were supplied at 450 ºC on the *a*-axis-oriented α-Fe layer, the Fe layer was entirely nitrided to form γ'-Fe_4N. The M_s value is in good agreement with that of bulk γ'-Fe_4N. Using this technique, we were able to grow *a*-axis-oriented Fe_4N/MgO/Fe MTJ. The probable method of formation of Fe_4N/MgO/Fe_4N MTJ was also discussed based on the XRD patterns. In the *M-H* curve of the MTJ structure measured at 280 K, a two-step hysteresis loop was observed, suggesting that two ferromagnetic layers were separated by a 1-nm-thick MgO barrier layer.

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Figure captions

Figure 1 θ-2θ XRD patterns of samples obtained after (a) 0, (b) 8, (c) 15, (d) 25 and (e) 30 min after supplying Fe(30 nm)/MgO with Fe and N. (f) θ-2θ XRD pattern obtained after 60 min after supplying Fe(7 nm)/MgO with Fe and N. (g) θ-2θ XRD pattern from N supply after 60 min on Fe(7 nm)/MgO. Inserts show the RHEED patterns obtained at each growth stage.

Figure 2 Schematic illustrations of (a) α-Fe on MgO(001) and (b) γ'-Fe_4N on Fe/MgO(001). RHEED observation was performed along the [100] azimuth of MgO.

Figure 3 *M-H* curve of the γ'-Fe_4N(80 nm) layers on MgO measured at 280 K with *H* parallel to the sample plane.

Figure 4 θ-2θ XRD patterns of (a) before and (b) after the growth of MTJ. (a) and (b) for MgO(1 nm)/Fe(100 nm), and Fe_4N/MgO/Fe MTJ, respectively.

Figure 5 *M-H* curve of the Fe_4N/MgO/Fe MTJ measured at 280 K with *H* parallel to the sample plane.