Growth of highly-oriented crystalline α-Fe/AlN/Fe_3N trilayer structures on Si(111) substrates by molecular beam epitaxy

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Abstract

We have realized highly-oriented nitride-based α-Fe/AlN/Fe_3N ferromagnetic hybrid structures on Si(111) substrates by molecular beam epitaxy using AlN/SiC intermediate layers. A two-step hysteresis loop, typically observed in magnetic tunneling junctions, was clearly observed in magnetization versus magnetic field measurements. This result indicates the formation of ferromagnetic α-Fe and Fe_3N layers separated by 8-nm-thick AlN layers over approximately 1cm^2 areas, and also shows the difference in coercive field between the two ferromagnetic layers.

Keywords: B3. magnetic tunnel junction; B2. Fe_3N; B2. α-Fe; B2. AlN; A3. MBE; A1. SQUID

1. Introduction

Spintronics, a new research field of electronics based on the combination of magnetic and semiconducting materials, has been attracting much attention. In particular, the tunnel magnetoresistance (TMR) effect in magnetic tunnel junctions (MTJs), which consist of two ferromagnetic layers separated by an insulating layer, has been extensively studied [1,2]. Magnetoresistive random-access memory (MRAM) is a device which utilizes the TMR effect [3]. An MRAM is a nonvolatile memory, and is also believed to have high integrity in a dynamic random-access memory (DRAM) as well as high-speed operation in a static random-access memory (SRAM). To achieve a Gbit-scale MRAM, TMR ratios exceeding 150 % and output voltages over 190 mV are required [4]. One way to overcome these difficulties is to grow crystalline MTJs, in which coherent electron tunneling without spin scattering can be expected [5,6]. Giant TMR ratios have been achieved in MTJs consisting of an MgO barrier layer and Fe-Co ferromagnetic layers [7], and further efforts have been made in this material system [8]. We have been looking for other ferromagnetic and semiconducting materials, and in particular, have been paying attention to nitride-based materials. Iron nitrides are very interesting due to their special features such as high hardness, chemical inertness, and high electrical conductivity [9-13]. Among them, ferromagnetic Fe_3N, Fe_4N and $Fe_{16}N_2$ have been extensively studied for application in high-density magnetic recording heads and media [14,15]. Very recently, Kokado *et al.* have predicted highly spin-polarized transport in Fe_4N

[16]. On the other hand, nitride semiconductors such as GaN and AlN are very important materials for future electron and optical devices. They also possess high hardness and chemical inertness. However, there have been no reports so far on the epitaxial growth of ferromagnetic iron-nitrides on Si substrates, and nitride-based MTJs. We have succeeded in the epitaxial growth of *c*-axis-oriented hexagonal Fe_3N films on Si(111) substrates by molecular beam epitaxy (MBE) using AlN/3C–SiC intermediate layers [17,18]. It was found that the AlN layers work as a template for Fe_3N overlayers, and that the AlN epitaxial layers are likely to form on 3C-SiC.

In this paper, we report on the formation of highly-oriented nitride-based crystalline α-Fe/AlN/Fe_3N trilayer structures on Si substrates by MBE for the first time. The magnetic properties of the films were also discussed.

2. Experimental procedure

Prior to the formation of α-Fe/AlN/Fe_3N trilayer structures, the growth conditions of highly-oriented α-Fe films on AlN layers were optimized using Si(111) substrates covered with AlN/3C-SiC layers as follows. First, approximately 3-nm-thick 3C-SiC buffer layers were grown through the carbonization of the Si surface using cracked C_3H_8 at 900ºC [19,20]. Then, 10-nm-thick *c*-axis-orientated AlN layers were grown at 900ºC using di-methyl-aluminum hydride (DMAH) as an Al source and NH_3 as a N source [21]. After that,

40-nm-thick α-Fe layers were grown at several different temperatures using iron-pentacarbony ($Fe(CO)_5$) as an Fe source. For comparison, the formation of α-Fe films was also tried directly on Si(111) substrates or Si substrates capped with 3C-SiC layers in the same manner.

The formation of α-Fe/AlN/Fe_3N trilayer structure was performed as follows. First, 30-nm-thick Fe_3N ferromagnetic layers were grown epitaxially on AlN/3C-SiC intermediate layers by MBE. The detailed growth conditions were reported in our previous papers [16,17]. Then, 8-nm-thick AlN barrier layers were grown by an RF magnetron sputtering method at 100ºC. The AlN layers were formed by sputtering an Al target in the mixture of Ar and N_2 atmosphere. The formation of (0001)-oriented AlN layer by this method was confirmed by X-ray diffraction (XRD) not for the 8-nm-thick AlN but for much thicker AlN layers. The deposition rate of AlN is approximately 6.6 nm/min, and the thickness of the AlN barrier layer was thus determined using this deposition rate. Finally, 40-nm-thick α-Fe layers were grown at 350ºC.

The crystallinity of the grown layers was characterized by reflection high-energy electron diffraction (RHEED) and XRD. All the RHEED patterns were taken from the [1-10] azimuth of Si. Surface morphology was observed by atomic force microscopy (AFM). A superconducting quantum interference device (SQUID) magnetometer was used to measure the magnetic properties of the samples.

3. Result and discussions

3.1 Formation of α-Fe on AlN

Figures 1(a) and 1(b) show RHEED patterns of the 3C-SiC and AlN layers, respectively. Figures 1 (c) -1(f) show RHEED patterns of α-Fe layers grown at different temperatures on the AlN/3C-SiC intermediate layers. The streaky RHEED patterns were observed for 3C-SiC and AlN layers as shown in Figs. 1(a) and 1(b). In contrast, the ring pattern was observed after the supply of $Fe(CO)_5$ at low temperatures as shown in Figs. 1(c) and 1(d). With increasing the growth temperature, the diffraction spots appeared as shown in Figs. 1(e) and 1(f). These results indicate that the crystallinity of α-Fe layers was improved when the growth temperature was raised. Figure 2 shows θ-2θ XRD patterns of these samples. The diffraction peak of only α-Fe (110) was observed when the growth temperature becomes equal to or higher than 300ºC, indicating that highly (110)-oriented α-Fe was formed. The diffraction spots observed in Figs. 1(e) and 1(f) were composed of two sets of diffraction patterns of α-Fe, open and closed circles, as shown in Fig. 3(a). These patterns are thought to be due to three possible epitaxial variants for (110)-oriented α-Fe layers on AlN(0001) as shown in Figs. 3(b)-3(d). The diffraction spots denoted by closed circles in Fig. 3(a) can be explained by α-Fe layers with the relationship as shown in Figs. 3(b) and 3(c). On the other hand, the diffraction spots denoted by open circles are attributed to α-Fe layers as shown in

Fig. 3(d).

We also tried to form highly-oriented α-Fe layers directly on Si(111) substrates for comparison; however, the Fe reacted with Si and thereby iron silicides such as FeSi, β-$FeSi_2$ and α-$FeSi_2$ were formed in spite of α-Fe layers. Highly-oriented α-Fe layers were difficult to form even on 3C-SiC layers as shown in Fig. 4. Figure 4 shows the θ-2θ XRD patterns after the supply of $Fe(CO)_5$ onto the 3C-SiC layers at various temperatures. The diffraction peak of α-Fe could hardly be confirmed. When the deposition temperature was 275ºC, the diffraction peak of α-Fe(110) was observed; however, the peak intensity was very small. On the basis of these results, it can be said that the introduction of AlN layers is a very effective way to form highly-oriented α-Fe layers on Si.

3.2 Formation of α-Fe/AlN/Fe_3N trilayer structure

Next, we tried to form α-Fe(40 nm)/AlN(8 nm)/Fe_3N(30 nm) trilayer structure. Figures 5(a), 5(b) and 5(c) show RHEED patterns observed after the growth of Fe_3N, AlN and α-Fe layers, respectively. The diffraction spots of *c*-axis-oriented hexagonal Fe_3N were observed as shown in Fig. 5(a), indicating that the monocrystalline Fe_3N was formed. The root-mean-square (rms) roughness value of the Fe_3N measured by AFM was 6.1 nm. The thickness of the Fe_3N layer was approximately 30 nm. Thus, the surface of the Fe_3N is not smooth, and further studies are necessary to obtain a smooth surface of Fe_3N. The thickness of

the AlN barrier layer was therefore determined to be thick enough (8 nm) to separate the Fe_3N layer from α-Fe overlayers in this work. The crystallinity of this AlN barrier layer is not good enough compared to that formed at 900ºC shown in Fig. 1(b). We think that this is due to the low temperature formation of AlN layers. Figure 6 shows the θ-2θ XRD pattern of samples after the formation of (a) Fe_3N layers and (b) trilayer structure. We can see the diffraction peaks of AlN(0002) as well as Fe(110) in Fig. 6(b). The RHEED pattern of the α-Fe layer shown in Fig. 5(c) is a ring pattern. This means that a polycrystalline α-Fe layer was grown. The difference in RHEED pattern of α-Fe between Figs. 1(e, f) and Fig. 5(c) is attributed to the difference in crystallinity of AlN underlayers.

The two solid lines in Fig. 7 show the magnetization versus magnetic field (*M-H*) curves measured at 280 K after the growth of the Fe_3N layer and the trilayer structure. The external *H* was applied parallel to the sample surface. We can see a clear two-step structure for the trilayer structure, which is usually observed in MTJs. This is attributed to the difference in coercive field, *H*c, between the α-Fe and Fe_3N ferromagnetic layers, showing the successful formation of ferromagnetic α-Fe and Fe_3N layers separated by the AlN layer over the entire sample areas of approximately $1cm^2$. This *M-H* curve is the sum of the *M-H* curve of the α-Fe (broken line) and that of the Fe_3N (dotted line) in the trilayer structure. The saturation magnetization, *M*s, of α-Fe, which is 1737 emu/cm^3 [13], explains the broken line well. The *M*s value for the Fe_3N layer in the dotted line also agrees well with that for the Fe_3N

in the solid line. However, the *Hc* value in the Fe_3N decreased from 150 Oe in the solid line to 45 Oe in the dotted line. We think that this is because the crystallinity of the Fe_3N layer changed during the formation of the AlN and subsequent α-Fe overlayers. The electrical properties of the trilayer structure are now under investigation. We think that the formation of the hybrid structures presented in this work is an important step toward realizing nitride-based MTJs.

4. Conclusion

Highly (110)-oriented α-Fe layers were formed on AlN layers at temperatures equal to or higher than 300ºC using $Fe(CO)_5$ as an Fe source. Using this growth condition, we next formed crystalline α-Fe(40 nm)/AlN(8 nm)/Fe_3N(30 nm) trilayer structures on Si(111) substrates using the AlN/SiC intermediate layers, where the α-Fe was (110)-oriented and the Fe_3N was *c*-axis-oriented. In the *M-H* measurements, a two-step hysteresis loop was clearly observed at 280 K, meaning that the two ferromagnetic layers were separated by the AlN layer.

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158

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Figure captions

Figure 1 RHEED patterns taken after the growth of (a) 3C-SiC and (b) AlN layers. (c), (d), (e) and (f) are RHEED patterns of α-Fe layers grown at 250 ºC, 300 ºC, 350 ºC and 400 ºC, respectively, on the 3C-SiC/AlN intermediate layers.

Figure 2 θ-2θ XRD patterns of α-Fe layers grown on AlN/3C-SiC intermediate layers at various temperatures.

Figure 3 (a) RHEED pattern of the (110)-oriented α-Fe layers grown at 400ºC. The closed circles and open ones correspond to those obtained from α-Fe layers with the relationship of (b,c) and (d) on AlN(0001), respectively. The squares are diffraction spots obtained from all the three kinds of epitaxial variants.

Figure 4 θ-2θ XRD patterns taken after the supply of $Fe(CO)_5$ on 3C-SiC layers at various temperatures.

Figure 5 RHEED patterns of the (a) Fe_3N, (b) AlN and (c) α-Fe layers in the trilayer structures.

Figure 6 θ-2θ XRD patterns after the formation of (a) Fe_3N layers and (b) AlN and subsequent α-Fe layers.

Figure7 *M-H* curves measured at 280 K with *H* parallel to the sample plane. The solid lines are the *M-H* curves measured after the growth of the Fe_3N layers and trilayer structures. The broken and dotted lines are thought to correspond to the *M-H* curves of α-Fe and Fe_3N layers in the trilayer structures, respectively.