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Epitaxial growth of Fe_3O_4 on GaAs by gas flow sputtering

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In this study, the growth of magnetite (Fe_3O_4) thin films on GaAs(100) substrates by gas flow sputtering is investigated. The condition of substrate preheating before the growth of Fe_3O_4 affects the epitaxy of the Fe_3O_4 film to a great extent: an epitaxial film is obtained by substrate preheating in air, while polycrystalline films are obtained without substrate preheating and by substrate preheating in vacuo and in Ar. The formation of arsenic oxides may play a key role in the epitaxial growth. Reflection high-energy electron diffraction suggests that the epitaxial relationship is Fe_3O_4(100)//GaAs(100) and Fe_3O_4[001]//GaAs[011], and scanning electron microscopy shows that the film has a mosaic-like texture.
Key words: magnetite, epitaxial growth, gas flow sputtering, half-metal

1. INTRODUCTION

Developments are being made in spintronics, which takes advantage of spin degree of freedom as well as electrons. A spin transistor [1–3] is an active element and can be a key device in the spintronics. It comprises magnetic electrodes and a semiconductor channel, and a highly spin polarized material is favorable for the magnetic electrodes. Magnetite (Fe_3O_4) is a candidate for the electrode material because of its half-metallic nature, that is, complete spin polarization at the Fermi level. For the application of Fe_3O_4 to the spin transistor, a Fe_3O_4/semiconductor junction (for example, GaAs as the semiconductor) has to be fabricated.

Some studies have reported on the fabrication of a Fe_3O_4/GaAs junction, for example, fabrication by the pulsed laser deposition (PLD) of Fe_3O_4 on a GaAs substrate [4–6] and by the oxidation of an Fe epitaxial film on a GaAs substrate [7]. Fe_3O_4(100) epitaxial films were obtained successfully by the oxidation of Fe films; however, such films were not obtained by the direct deposition of Fe_3O_4 by PLD [4,6]. In Ref.5, (111)-oriented Fe_3O_4 films were obtained, leaving a possibility of epitaxial growth. Therefore, the fabrication of an epitaxial Fe_3O_4/GaAs junction is rather difficult, presumably due to the large lattice misfit between Fe_3O_4 and GaAs (~5%).

In our previous study, a Fe_3O_4 epitaxial thin film was successfully obtained on an insulator such as the MgO substrate by gas flow sputtering (GFS) [8,9]. GFS is based on hollow cathode discharge and sputtering at a high pressure around 100 Pa. The high pressure causes the mean free path of Ar atoms and sputtered atoms to be as short as 0.1 mm. Therefore, energetic particles lose their energies by collision with Ar atoms, thereby leading to the suppression of the damage of the deposited film. In this study, we report on the epitaxial growth of Fe_3O_4 on GaAs by GFS. In addition, the effects of preheating of the GaAs substrate are discussed.

2. EXPERIMENTAL

The deposition of Fe_3O_4 films on GaAs(100) substrates was carried out as follows. First, the substrate was ultrasonic-cleaned with acetone for 300 s, followed by rinsing it with distilled water. Next, the substrate was ultrasonic-cleaned with a cleaning solution for semiconductors, i.e., Semico clean 23 (Furuuchi Chemical Co.), for 300 s and again rinsed with distilled water. Finally, the surface of the substrate was blown with N_2 gas. After the cleaning, the substrate was transferred into the GFS chamber and preheated to 823 K for 1800 s in vacuo (4×10^{-4} Pa), in Ar (99.9999%), and in air prior to sputtering.

Figure 1 shows the schematic diagram of the GFS system used for the deposition of the Fe_3O_4 films. The sputtering target was an Fe (99.9%) tube with an inner diameter of 14 mm, outer diameter of 25 mm, and length of 50 mm. Ar gas (99.9999%, sputtering gas) was introduced into the chamber through the target, and O_2 (99.99%) reactive gas was supplied 30 mm downstream from the target. The sputtering was carried out under the following conditions: base pressure of 4×10^{-4} Pa, pressure of 130 Pa for sputtering, target-to-substrate separation of 100 mm, discharge power of 300 W, Ar gas flow rate of 0.51 $Pa \cdot m^3/s$, oxygen flow rate of 3.0×10^{-4} $Pa \cdot m^3/s$, and substrate temperature T_S in the range

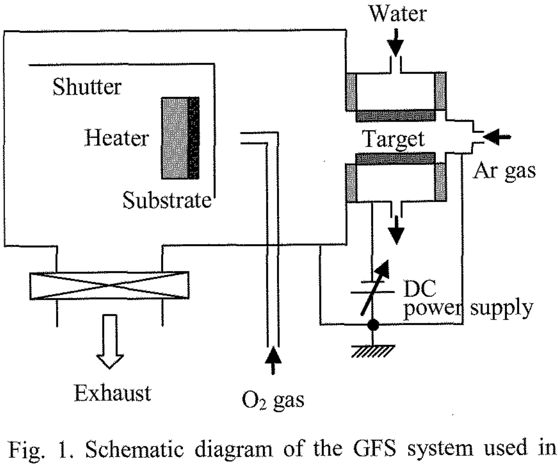

Fig. 1. Schematic diagram of the GFS system used in this study.

573–723 K during sputtering. The film thickness was approximately 200 nm.

After the sputtering, the film was removed from the chamber and examined as follows. The crystal structure and out-of-plane crystal orientation were evaluated by using X-ray diffraction (XRD, θ-2θ scan, Cu Kα radiation). The in-plane crystal orientation was evaluated by using reflection high-energy electron diffraction (RHEED) with an acceleration voltage of 20 kV. The surface morphology was evaluated by using scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

First, we deposited Fe_3O_4 films at T_S = 673 K after the preheating of the GaAs substrates under several conditions. Figure 2 shows the XRD patterns of the films without substrate preheating and with substrate preheating in vacuo, in Ar, and in air. The samples without preheating and with preheating in vacuo and in Ar show Fe_3O_4 311, 222, 400, and 511 peaks. This confirms that Fe_3O_4 was deposited; however, the crystals were not oriented. On the other hand, the sample with preheating in air shows only the Fe_3O_4 400 peak, and its intensity is very high. This indicates the (100) orientation to the substrate. Therefore, substrate preheating in air is the best alternative under such preheating conditions. The important point is that it is in contrast to the general preparation conditions of the GaAs substrate, wherein heating is carried out in vacuo to eliminate the surface oxide layer [7,10]. Hereafter, we focus on preheating in air.

The effect of the substrate temperature for sputtering on the crystal orientation was investigated. Substrate preheating was carried out in air. Figure 3 shows the XRD patterns of the films deposited at T_S = 573–723 K. For all the films, a sharp 400 peak of Fe_3O_4 was observed, indicating that all the films are (100)-oriented and possibly epitaxial films. The peak intensity at T_S = 673 K is particularly high. Figure 4 shows the RHEED patterns of the films. The film deposited at T_S = 573 K shows rings as well as spots, indicating that this film is slightly oriented yet polycrystalline. The film deposited at T_S = 623 K also shows polycrystalline rings, although they are very weak. On the other hand, the films deposited at T_S = 673 K and 723 K show only spots, indicating that the crystallites are oriented. The film surfaces are slightly rough as concluded from the fact that they do not exhibit streak patterns.

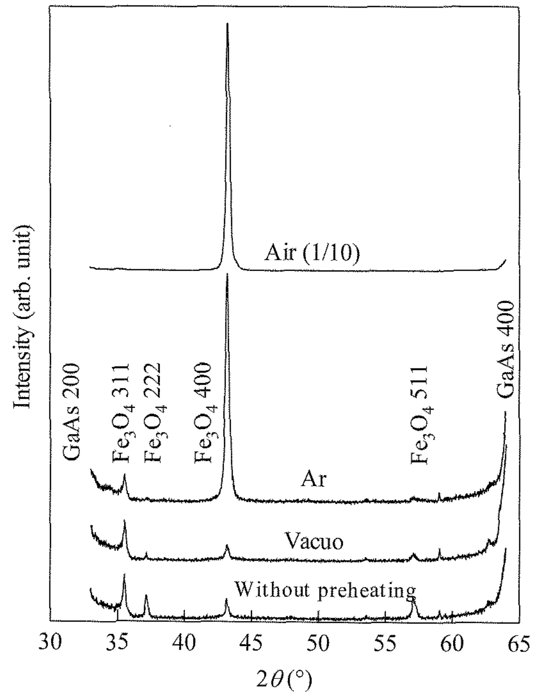

Fig. 2. XRD patterns of Fe_3O_4 films without substrate preheating and with preheating in vacuo, in Ar, and in air. The intensity of the film with preheating in air is multiplied by 1/10 for clarity. T_S for magnetite deposition was 673 K.

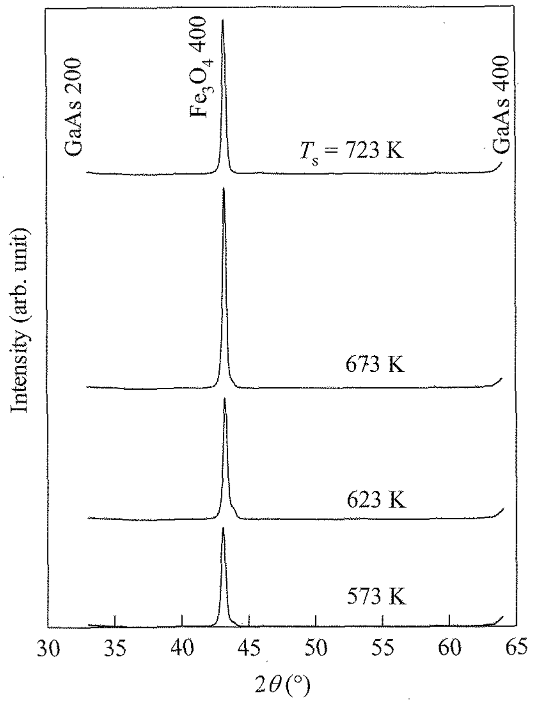

Fig. 3. XRD patterns of Fe_3O_4 films deposited at different T_S values. The substrates were preheated in air.

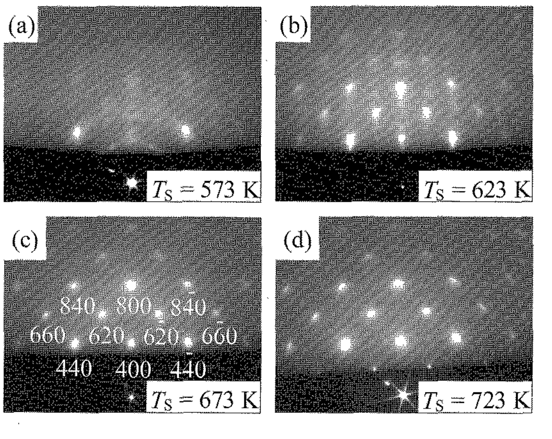

Fig. 4. RHEED patterns of Fe_3O_4 films deposited at different T_S values. The substrates were preheated in air. The incident electron beam was along the [011] direction of GaAs.

We discuss the epitaxial relationship between the Fe_3O_4 film and the GaAs substrate for the film deposited at T_S = 673 K, which shows the highest peak intensity in XRD. The diffraction indices are shown in Fig. 4(c). The incident electron beam is along the [001] direction of Fe_3O_4. Since the incident electron beam direction is also along the $[01\bar{1}]$ direction of the GaAs substrate, the directions [001] of Fe_3O_4 and $[01\bar{1}]$ of GaAs are parallel to each other. Therefore, the epitaxial relationship is Fe_3O_4(100)//GaAs(100) and Fe_3O_4[001]//GaAs$[01\bar{1}]$. This relationship is in agreement with that reported by another group [7].

The surface morphologies of the Fe_3O_4 films were evaluated by SEM. Figure 5 shows the SEM images of the films deposited at T_S = 573–723 K. The grain size and shape of the films deposited at T_S = 573 and 623 K are not uniform. The film deposited at T_S = 673 K has a mosaic-like texture, i.e., oriented square grains with a uniform size. This implies that the film has a good crystal orientation, and it is in good agreement with the obtained RHEED patterns. Although the film deposited at T_S = 723 K also shows distinct grains, their shapes are not uniform. This may correspond to the additional spots observed in the RHEED pattern (Fig. 4(d)).

In summary, polycrystalline Fe_3O_4 films were obtained without substrate preheating and by substrate preheating in vacuo and in Ar. On the other hand, an epitaxial Fe_3O_4 film was obtained by preheating the substrate in air. Further, we discuss the reason why the preheating of the GaAs substrate in air is suitable for the epitaxial growth of Fe_3O_4. Figures 6 and 7 show the XRD and RHEED patterns of the GaAs substrates without preheating and with preheating in vacuo, in Ar, and in air. The XRD pattern of the GaAs substrate without preheating shows some phases other than GaAs. The RHEED pattern of the substrate shows streaks, indicating that the surface of the substrate is very flat. The preheating in vacuo or in Ar reduces the quantity of the impurity phases, as shown in the XRD patterns. However, the surfaces of the substrates become rough by surface reconstruction, as confirmed from the RHEED patterns. The preheating in air promotes the growth of arsenic oxides. The RHEED

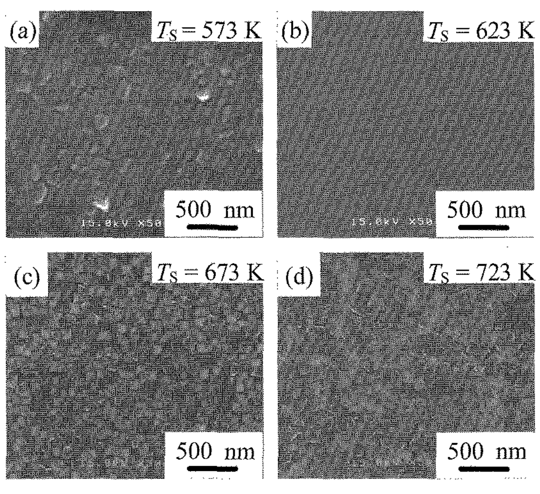

Fig. 5. SEM images of Fe_3O_4 films deposited at different T_S values. The substrates were preheated in air.

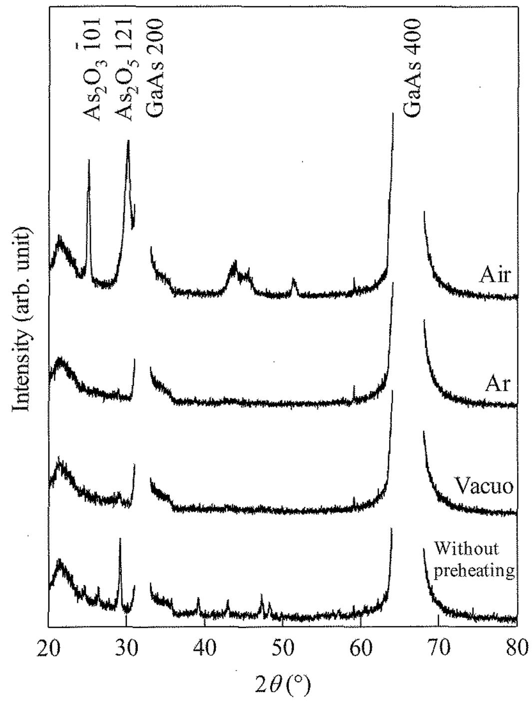

Fig. 6. XRD patterns of GaAs(100) substrates without preheating and with preheating in vacuo, in Ar, and in air.

pattern shows weak spots, indicating a poor crystallinity. In general, a flat surface and lattice matching with the depositing film are required for epitaxial growth. However, for a Fe_3O_4/GaAs system, the lattice mismatch between Fe_3O_4 and GaAs is rather large, as mentioned in the introduction. Therefore, the arsenic oxides formed by the preheating in air may serve as a good buffer layer for the epitaxial growth of Fe_3O_4. Further, the optimization of conditions such as temperature and time during preheating in air may improve the flatness of the Fe_3O_4 film. The effect of the arsenic oxide layer on the spin injection properties would be a topic of interest.

4. CONCLUSION

An epitaxial Fe_3O_4 film can be obtained on the

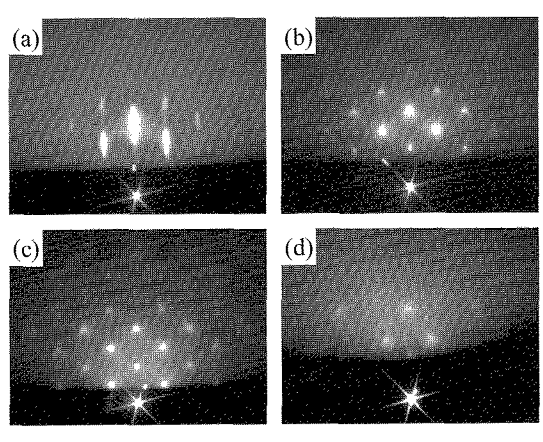

Fig. 7. RHEED patterns of GaAs(100) substrates with (a) no preheating, (b) preheating in vacuo, (c) in Ar, and (d) in air. The incident electron beam was along the $[01\bar{1}]$ direction of GaAs.

GaAs(100) substrate by using GFS. The suitable condition for substrate preheating is preheating in air, which is in contrast to the general conditions. Preheating in vacuo or in Ar makes the Fe_3O_4 film polycrystalline. The epitaxial relationship is Fe_3O_4(100)//GaAs(100) and Fe_3O_4[001]//GaAs[011], which is in agreement with the reported relationship.

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REFERENCES

[1] D. J. Monsma, J. C. Lodder, Th. J. A. Popma and B. Dieny, *Phys. Rev. Lett.*, **74**, 5260–5263 (1995).

[2] S. van Dijken, X. Jiang and S. S. P. Parkin, *Appl. Phys. Lett.*, **80**, 3364–3366 (2002).

[3] S. Sugahara and M. Tanaka, *Appl. Phys. Lett.*, **84**, 2307–2309 (2004).

[4] E. J. Preisler, J. Brooke, N. C. Oldham and T. C. McGill, *J. Vac. Sci. Technol. B*, **21**, 1745–1748 (2003).

[5] R. Prakash, R. J. Choudhary, L. S. Sharath Chandra, N. Lakshmi and D. M. Phase, *J. Phys.: Condens. Matter.*, **19**, 486212–486220 (2007).

[6] M. L. Parames, Z. Viskadourakis, M. S. Rogalski, J. Mariano, N. Popovici, J. Giapintzakis and O. Conde, *Appl. Surf. Sci.*, **253**, 8201–8205 (2007).

[7] Y. X. Lu, J. S. Claydon, Y. B. Xu, S. M. Thompson, K. Wilson and G. van der Laan, *Phys. Rev. B*, **70**, 233304/1–233304/4 (2004).

[8] K. Ishii, T. Satomi and A. Irino-uchi, *Trans. Mater. Res. Soc. Jpn.*, **28**, 1113–1116 (2003).

[9] H. Sakuma, S. Sato, R. Gomimoto, S. Hiyama and K. Ishii, *IEEJ Trans.*, **2**, 431–435 (2007).

[10] J. Saito, K. Nanbu, T. Ishikawa and K. Kondo, *J. Appl. Phys.*, **63**, 404–409 (1988).

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