Formation of $\text{Fe}_3\text{O}_4/\text{GaAs}$ Heterostructure via Surface Oxidation of GaAs Substrate

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Abstract

In our previous study, we found that magnetite is epitaxially grown on GaAs substrate pre-annealed in air. While the formation of an oxidized layer is confirmed on GaAs by electron microscopy, the composition and crystal structure was unknown. In this study, the oxidized layer is revealed to be $\beta\text{-Ga}_2\text{O}_3$, of which (100) plane is parallel to the substrate plane by x-ray and electron diffractions. It disappears during the sputter deposition of magnetite on it, and a clear $\text{Fe}_3\text{O}_4/\text{GaAs}$ interface is formed. The epitaxial relationship of the $\text{Fe}_3\text{O}_4/\text{GaAs}$ heterostructure is cube-on-cube in contrast to that fabricated by a conventional method.

Key Words: Magnetite, GaAs, Epitaxial growth, X-ray diffraction, Transmission electron microscopy

I. INTRODUCTION

Magnetite (Fe_3O_4) is a half-metallic material, and the electron is highly spin-polarized at the Fermi level. Another attractive property of Fe_3O_4 is a high Curie temperature of 585°C [1]. A hybrid structure of Fe_3O_4 and a semiconductor such as GaAs is expected to perform as a spin field-effect transistor or spin light-emitting diode. However, only a few papers [2] report on the successful fabrication of such $\text{Fe}_3\text{O}_4/\text{GaAs}$ devices. This is mainly due to a difficulty in the growth of Fe_3O_4 on GaAs. The $\text{Fe}_3\text{O}_4/\text{GaAs}$ heterostructure is conventionally fabricated by the following process. It is well known that iron (Fe) is epitaxially grown on GaAs. The Fe epitaxial thin film is then oxidized, resulting in the formation of Fe_3O_4 film [1,3]. Further Fe_3O_4 may be deposited on the oxidized Fe_3O_4 [2].

In our previous paper [4], we reported another method to fabricate $\text{Fe}_3\text{O}_4/\text{GaAs}$ heterostructure: Fe_3O_4 is deposited on the GaAs substrate pre-annealed in air. Although the pre-annealing in air is expected to form a kind of oxide on the GaAs surface, the chemical composition and crystal structure have not been analyzed. This paper describes the results of analyses for the surface oxidized layer and $\text{Fe}_3\text{O}_4/\text{GaAs}$ heterostructure thus formed.

II. EXPERIMENT

GaAs(001) substrates were ultrasonic-cleaned with a cleaning solution for semiconductors, i.e., Semico clean 23 (Furuuchi Chemical Co.), for 300 s and rinsed with distilled water. Then the substrates were pre-annealed at 550°C for 30 min in air. Fe_3O_4 is deposited on the pre-annealed GaAs substrates by gas flow sputtering [5]. The sputtering target was Fe tube with an inner diameter of 14 mm. The chamber was evacuated to below 5×10^{-4} Pa prior to sputtering. Ar gas with a flow rate of 300 sccm was introduced to the chamber through the target, and the pressure was kept at 130 Pa during sputtering. O_2 reactive gas with a flow rate of 0–0.18 sccm was supplied 30 mm downstream from the target.

Fig. 1 (a) Cross-sectional TEM image and (b-e) element maps. The sputter deposition was performed without O_2 gas flow. (f) Electron diffraction pattern of oxidized layer. Major zone axis is [010].

Fig. 2 (a) XRD patterns of GaAs substrate pre-annealed in air. The x-ray scattering vectors Q are parallel to [001], [101], and [111] of GaAs. (b) A crystal orientation suggested by x-ray and electron diffractions (viewed from top surface). The black lines indicate unit cells.

Discharge current was DC 1 A. The substrate was kept at 400°C or 500°C during sputtering. The film thickness was approximately 200 nm.

The pre-annealed substrate and that deposited with Fe_3O_4 are evaluated by using transmission electron microscopes (TEM) and an x-ray diffractometer (XRD) with an Eulerian cradle (PANalytical X'Pert Pro MRD). For TEM analysis, the incident electron beam is along the [110] direction of GaAs. For 2θ - θ XRD measurements, the samples were set so that the [110] direction of GaAs is in the goniometer circle. The Eulerian cradle was set at three sets of angles; $\phi = \chi = 0^\circ$, $\phi = \chi = 45^\circ$, and $\phi = 0^\circ$, $\chi = 54.74^\circ$, which correspond x-ray scattering vectors (Q) parallel to [001], [101], and [111] of GaAs, respectively.

III. RESULTS AND DISCUSSION

Figure 1(a) shows TEM image of a cross-section of the film, for which O_2 gas was not supplied during sputtering. An oxidized layer with a thickness of about 50 nm remains at the interface between the deposited film and GaAs. The composition of the oxidized layer was analyzed by energy dispersive x-ray spectroscopy. From the element maps shown in Figs. 1(b-e), the oxidized layer consists of Ga and O, while As and Fe are not present. The atomic ratio of Ga to O is 0.59. It is also noted that As is precipitated under the oxidized layer. However, the oxidized layer is continuous on the boundary of GaAs and As. Figure 1(f) shows electron diffraction pattern of the oxidized layer. Most of diffraction spots are identified as those of monoclinic β - Ga_2O_3 . The major zone axis is [010], although some variants exist. Figure 2 shows the XRD patterns of GaAs substrate pre-annealed in air. The x-ray scattering vectors are parallel to [001], [101], and [111] of GaAs. 400 and 403 peaks of β - Ga_2O_3 are found. The crystal orientation expected from the electron and x-ray diffractions is (100) parallel to the substrate plane, and some variants may

Fig. 3 (a) TEM image of $\text{Fe}_3\text{O}_4/\text{GaAs}$ interface. The sample was fabricated with O_2 gas flow rate of 0.18 sccm. (b,c) Electron diffraction patterns of Fe_3O_4 and GaAs, respectively. The diffraction patterns were acquired for both areas approximately 20 nm away from the interface with a beam size of approximately 10 nm. Both zone axes are [110].

Fig. 4 (a) XRD patterns of $\text{Fe}_3\text{O}_4/\text{GaAs}$ sample fabricated with O_2 gas flow rate of 0.18 sccm. (b) Crystal orientation suggested by x-ray and electron diffractions (viewed from top surface).

exist for in-plane orientation. Although the symmetry of the crystal structure of $\beta\text{-Ga}_2\text{O}_3$ is low in contrast to the cubic GaAs, (100) plane of $\beta\text{-Ga}_2\text{O}_3$ has a quasi-four-fold symmetry as shown in Fig. 2(b). It is also noted that XRD collects macroscopic information over the sample, while electron diffraction is for a nanoscale part.

In our previous report [6], it was shown by scanning electron microscopy that the oxidized layer disappears, if the sputter deposition is performed with O_2 gas flow rate above 0.12 sccm. It is verified by TEM as shown in Fig. 3(a). The interface between Fe_3O_4 and GaAs is clear, and no obvious interface layer is found. Diffraction experiments (electron diffraction pattern shown in Fig. 3(b) and XRD patterns shown in Fig. 4(a)) also indicate that almost no impurity phase exists. The epitaxial relationship is cube-on-cube as shown in Fig. 4(b) in contrast to that of $\text{Fe}_3\text{O}_4/\text{GaAs}$ heterostructure fabricated by the conventional method, in which a unit cell of Fe_3O_4 is rotated 45° relative to that of GaAs to decrease lattice mismatch. The cube-on-cube relationship results in a fairly large lattice mismatch of 48%, which may be relaxed by forming a mosaic structure [6]. Such a structure is actually observed on the surface of Fe_3O_4 layer [4]. It is an open question how Ga is incorporated in the Fe_3O_4 layer. Abe et al. reported that small addition of Ge improves the chemical stability of Fe_3O_4 [7], and the effect of Ga on the formation of Fe_3O_4 should be investigated in the future.

IV. CONCLUSIONS

The oxidized layer formed on GaAs surface by pre-annealing in air is $\beta\text{-Ga}_2\text{O}_3$, of which (100) plane is parallel to the substrate plane. After the deposition of Fe_3O_4 on the pre-annealed GaAs substrate, $\beta\text{-Ga}_2\text{O}_3$ disappears and $\text{Fe}_3\text{O}_4/\text{GaAs}$ heterostructure is formed. The epitaxial relationship is cube-on-cube.

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