Growth of mixed phased films of $\gamma$-Fe$_2$O$_3$ and half metallic Fe$_3$O$_4$ using (100) MgO/Fe under layer for spin electronic devices

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Abstract. Half metallic magnetite films using (100) MgO/Fe under layer deposited at room temperature were prepared using facing targets sputtering method. X-ray diffractometry and TEM analyses confirmed epitaxial growth of (100) oriented Fe$_3$O$_4$ layer on (100) oriented MgO under layer prepared on 5nm-thick Fe buffer layer on glass substrates. Resistivity analyses clarified that higher oxygen partial pressure caused higher oxidation of Fe ions in the films which tend to result in $\gamma$-Fe$_2$O$_3$. Substrate heating is effective to improve crystallinity and magnetic properties of Fe$_3$O$_4$ film. Oxygen partial pressure of 7.5%, substrate temperature of 150 ºC and sputtering discharge current of 0.45A was suitable to prepare magnetite Fe$_3$O$_4$ film with (100) preferential orientation and good magnetic properties.

1. Introduction

Half metallic materials which have only minority spins in the density of states at Fermi level are desirable for spintronic devices because of their theoretical 100% spin polarization. Among these materials, Fe$_3$O$_4$ has gained an extraordinary interest due to its relatively high Curie temperature (858K) which is suitable for room temperature operation of spintronic devices[1][2]. Meanwhile the tunnelling barrier in magnetic tunnel junction (MTJ) has been developed from amorphous Al$_2$O$_3$ layer to (100) oriented MgO layer to achieve high TMR ratio [4]. The epitaxial multilayer that takes the advantages of both half-metallic Fe$_3$O$_4$ layer and (100) oriented MgO layer is expected to get a much greater TMR ratio [3]. Thus magnetite/MgO layers have potential applications in various magneto-resistive devices such as MTJs, spin filters and so on. In our study, we aim to prepare an epitaxial Fe$_3$O$_4$ (100) oriented film using MgO (100) oriented film as under layer (lattice misfit: ~ 0.3%) prepared on a Fe buffer layer on glass substrates.

2. Experiment

All the films (including Fe oxide single layers, MgO/Fe bilayers, Magnetite/MgO/Fe trilayers) have been prepared on glass substrates using facing targets sputtering (FTS) method. Background pressure was less than 10$^{-6}$ Torr. Fe and Mg disks with diameter of 10 cm were used as targets. For MgO and magnetite layers, O$_2$ is added into the chamber to achieve reactive sputtering during the deposition.

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The MgO/Fe under layers were deposited without substrate heating, while the third Fe oxide layers were grown at substrate temperature ranging from room temperature (R.T.) to 200 °C. Structural characterizations of thin films were performed by X-Ray Diffractionometry (XRD) and Transmission Electron Microscopy (TEM). Analysis of magnetic and electrical properties was done by using Vibrating Sample Magnetometer (VSM) and four-point probe method, respectively.

3. Results and Discussion

3.1. Effect of Fe buffer layer and MgO under layer on Fe oxide layer

We tried to find the appropriate preparation conditions of MgO (100) oriented layers with Fe buffer layer on glass substrate at room temperature by changing different deposition parameters and the thickness of Fe layer. Figure 1 shows the out-of-plane XRD diagrams of MgO/Fe films for various thicknesses of Fe buffer layers. Values on the right side indicate the thickness of Fe layer. If there is no Fe buffer layer, MgO layer exhibits (220) preferential orientation. While the (220) orientation disappeared when 1 nm-thick Fe buffer layer was prepared but there is still no MgO (100) orientation. According to the diagram, MgO layer exhibits (100) orientation only for the cases of 5 nm and 30 nm-thick Fe buffer layers. MgO (100) oriented film can be grown epitaxially on Fe layer with (100) preferential orientation in the 5nm-thick and 30nm-thick Fe layers, since the Fe (200) peak can be observed in the films with 5nm-thick and 30nm-thick Fe layers. After the confirmation of MgO (100) orientation for the MgO/Fe under layer, we fabricated Fe oxide thin films on MgO/Fe bilayers as shown in figure 2. Although the Fe oxide single layer showed (311) orientation the multilayer exhibits strong (100) orientation. Thus the under layer is very effective to change the orientation of Fe oxide layer. The epitaxial growth of Fe oxide layer on MgO/Fe under layer is achievable.

3.2. TEM observation

TEM analyses were performed on cross sectional specimens to study the structure and the morphology of the interface between under layer and Fe oxide layer. 100nm-thick Fe-oxide films were prepared at 0.57 Pa of Ar and O₂ mixture gas with 7.5% of O₂ flow rate. Figure 3 shows the electron diffraction (ED) patterns and the TEM photographs of the Fe₃O₄ films deposited at R.T. and 150 °C on MgO(20nm)/Fe(5nm) under layer deposited at room temperature. The direction of electron beam is perpendicular to the plane of paper. In ED observation, 10 μm- area selected aperture slot was used. The regions observed in ED patterns were all most same as that in Bright field patterns. (a) - (d) and (e) - (h) correspond to the Fe₃O₄ films deposited at R.T. and 150 °C, respectively.

Figure 1. XRD diagrams of MgO/Fe films with different thickness (X nm) of Fe buffer layer.

Figure 2. XRD diagrams of Fe oxide single layer, Fe oxide layer/MgO/Fe multilayer and MgO/Fe bilayer.
Figure 3. TEM images of 100nm-thick Fe$_3$O$_4$ layer on MgO/Fe under layer deposited at room temperature. (a) & (e): ED images; (b) & (f): Bright fields; (c) & (g): Dark fields; (d) & (h): HRTEMs. (a) - (d) and (e) - (h) correspond to the Fe$_3$O$_4$ films deposited at R.T. and 150 ºC, respectively.

ED images, Bright field images, Dark field images corresponding to (400) selected area diffraction and HRTEM images of those two films correspond to (a) & (e), (b) & (f), (c) & (g) and (d) & (h), respectively. ED image of R.T.-deposited Fe$_3$O$_4$ film shows very fine diffraction spots in the perpendicular direction to the film plane (labelled in the figure), as shown in figure 3 (a) which implies that the grains in R.T.-deposited Fe$_3$O$_4$ film are small and the vertical growth of the crystallites is not good. The film deposited at 150 ºC shows very obvious diffraction spots.
corresponding to Fe$_3$O$_4$ (400) and MgO (200) in the direction perpendicular to the film plane. Figure 3 (b) and (f) are bright field images and Figure (c) and (g) show dark field images corresponding to (400) selected diffraction spot of the films. Figure (f) and (g) also confirmed the better crystallinity of Fe$_3$O$_4$ layer deposited at substrate temperature of 150 ºC. Figure (d) and (h) are the HRTEM images of the specimens. For the magnetite layer, substrate temperature of 150 ºC is suitable to get good crystalline state. What is interesting, the thickness of MgO layer seems to be less than designed value (20nm), this maybe because the diffusion occurred during the process of TEM sample preparation. Ar ions with high energy sputtered to the very thin film of very small volume and then the temperature increased which may cause diffusion of Mg atoms.

3.3. Dependence of magnetic and electrical property on substrate temperature and O$_2$ partial pressure.

Figure 4 shows the XRD diagrams of the Fe-oxide films prepared at different substrate temperature on MgO/Fe underlayers which are deposited at R.T. All the Fe-oxide films were prepared at 0.57 Pa of Ar and O$_2$ mixture gas with 7.5% of O$_2$ flow rate. In the case of R.T. deposition, the diffraction line of Fe$_3$O$_4$ is so weak. Increase of substrate temperature around 150 ºC for the Fe-oxide film causes crystallization and (100) orientation of Fe$_3$O$_4$ crystallites. Further increase of substrate temperature above 200 ºC causes random growth of crystallites which reveals appearance of (311) diffraction line. VSM measurements allow us to estimate the value of the magnetization of the magnetic oxide films. Magnetization measured along the film plane for Fe-oxide layers prepared at different substrate temperatures deposited on MgO/Fe under layer were demonstrated in figure 5. It is regarded that substrate heating is effective to improve saturation magnetization $M_S$ and the coercive force $H_c$ of films due to the better crystallization caused by the increase of the deposition temperature for the Fe-oxide layers. $M_S$ values of 300, 210 and 175 emu/cc can be determined for the films grown at 150 ºC, 200 ºC and room temperature, respectively. The bulk value of Fe$_3$O$_4$ for $M_S$ is 471emu/cc. The reason for the decrease of $M_S$ may be ascribed to the existence of Anti-phase Boundaries (APBs) and $\gamma$-Fe$_2$O$_3$ phase [5].

**Figure 4.** XRD diagrams of 100nm-thick Fe$_3$O$_4$ layers deposited at various substrate temperature on MgO/Fe under layer.

**Figure 5.** M-H loops of 100nm-thick Fe$_3$O$_4$ layers deposited at various substrate temperatures on MgO/Fe under layer.
Figure 6. XRD diagram of Fe$_3$O$_4$ layer deposited on MgO/Fe under layer under different O$_2$ partial pressure ratio.

Figure 7. Resistivity of Fe oxide films as a function of O$_2$ partial pressure ratio for various deposition temperatures for Fe-oxide films.

Figure 6 shows XRD diagrams of Fe oxide/MgO/Fe multilayer with different O$_2$ partial pressure ratio. For the 4.5% of O$_2$ partial pressure ratio, Fe oxide layer has the dominant FeO phase. As the O$_2$ partial pressure ratio increases, it changed gradually to be Fe$_3$O$_4$ or $\gamma$-Fe$_2$O$_3$ phase. Since in our case we want to get (100) preferential oriented Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ phase and they have almost the same spinel structure, these two phases with same (100) preferential orientation can’t be distinguished easily through XRD. Figure 7 shows resistivity of Fe oxide films as a function of O$_2$ partial pressure ratio for various deposition temperatures for Fe-oxide films. The resistivity of Fe oxide films increases significantly with increasing O$_2$ partial pressure which indicate that higher O$_2$ partial pressure causes higher oxidation of Fe ions in the films which tend to result in higher resistivity. The film is oxidized transforming into maghemite $\gamma$-Fe$_2$O$_3$ film with higher resistivity. As the substrate temperature increases, the oxygen partial pressure at which the spinel ferrite is formed increases. At the same O$_2$ partial pressure, the lower substrate temperature causes higher oxidation. This may be because lower temperature can hold the O ions in the film while higher temperature can drive out O ions among the Fe ions. This tendency agrees with Ellingham diagram thermodynamics [6][7]. The bulk resistivity values of Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ are about $10^{-2}$ and $10^4$ Ω·cm, respectively. Thus it is probably that our film has a mixed phase of $\gamma$-Fe$_2$O$_3$ among Fe$_3$O$_4$ phase. In order to ensure the growth of Fe$_3$O$_4$, the next work is to get the temperature dependence of resistivity which can give the information of Verwey transition.

4. Conclusion
Fe$_3$O$_4$ (100) oriented film can be grown epitaxially on MgO (100) oriented under layer prepared on 5 nm-thick Fe buffer layer on glass substrates. Resistivity analyses confirmed that higher oxygen partial pressure causes higher oxidation of Fe ions in the films which tend to result in $\gamma$-Fe$_2$O$_3$. It is verified that substrate heating is effective to improve crystallinity and magnetic properties. However, high temperature above 200 °C causes diffusion of MgO which weaken Fe$_3$O$_4$ (100) orientation and growth indirectly. Experimental results showed that oxygen partial pressure of 7.5%, substrate temperature of 150 °C and sputtering discharge current of 0.45A was suitable to prepare magnetite Fe$_3$O$_4$ film with (100) preferential orientation, less density of $\gamma$-Fe$_2$O$_3$ mixed phase and good magnetic properties, which may be suitable for spintronic devices.

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