Change of Magnetic Properties and Structure in Fe₃O₄ Films on Si Substrates with Annealing Temperature

Sayeeduzzaman Syed¹*,1, Yasushi Endo¹*,2, Takanobu Sato¹*,1, Yoshio Kawamura¹ and Ryoichi Nakatani¹,2

¹Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan
²Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, Osaka 565-0871, Japan

We have investigated the magnetic properties and structure of Fe₃O₄ films on Si substrates before and after annealing at various temperatures, Tₐ. The saturation magnetization and the coercivity in the Fe₃O₄ films are observed at all Tₐ. They markedly increase with increasing Tₐ up to 873 K, and their values become maximum at Tₐ = 873 K. Furthermore, they slightly decrease above Tₐ = 873 K. The Fe₃O₄ phase mainly exists in the films at all Tₐ. In addition, the α-Fe₂O₃ phase (hematite) is also formed in the films above Tₐ = 873 K. On the basis of these results, it is found that the growth of Fe₂O₃ phase by annealing is mainly dominant in the change of magnetic properties in the Fe₂O₃ film up to Tₐ = 873 K and that the formation of α-Fe₂O₃ phase influences the change of magnetic properties in the Fe₂O₃ film above Tₐ = 873 K. [doi:10.2320/matertrans.MRA2007200]

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1. Introduction

Half-metallic materials with high spin polarization (100%) of the charge carriers at the Fermi level are very attractive as potential applications in spin electronics.¹ Several materials such as half Heusler alloys (NiMnSb)²,³ full Heusler alloys(Co₂MnSi)⁴,⁵ chromium dioxide (Cr₂O₃)⁶–⁹ pervoskites (La₀.₇Sr₀.₃MnO₃)¹⁰ and magnetite (Fe₂O₄)¹¹,¹² are well known to be half-metallic from both theoretical and experimental points of view. In particular, Fe₂O₄ has attracted much attention as a promising candidate for potential applications in spin electronics, because it has very high Curie temperature (850 K),¹³ as compared to that of other half-metallic materials.

Up to now, high oriented, epitaxial or polycrystalline Fe₂O₄ films have been obtained by various deposition techniques such as NO₂ or O₂ assisted molecular beam epitaxy (MBE),¹⁴,¹⁵ electron beam ablation,¹⁶ pulsed laser deposition from α-Fe₂O₃,¹⁷,¹⁸ or Fe₂O₄,¹⁹,²⁰ as a target, and reactive sputtering from an iron target with the argon and oxygen mixture gas flow.²¹–²³ It has been reported that as-deposited films have not only a Fe₂O₃ phase but also the other phase such as an iron or an iron oxide according to their deposition conditions.²²,²⁴,²⁵ It has also been found that epitaxial Fe₂O₄ films on the MgO show peculiar magnetic properties,²⁶,²⁷ and that a polycrystalline Fe₂O₄ film on the Si exhibits a large magnetoresistance of ~7.4% at room temperature.²⁸ Additionally, epitaxial Fe₂O₄ films have been prepared by post oxidation of an iron film.²⁹,³⁰ It has been demonstrated that the epitaxial Fe₂O₄ films on the GaAs show uniaxial magnetic anisotropy.³¹ However, there are few reports about the annealing effect on the magnetic properties and structure in Fe₂O₄ films,²²,²⁸ and its effect still remain unclear.

In the present study, we fabricate Fe₂O₄ films on Si (001) substrates at room temperature by ion beam sputtering, and systematically investigate the magnetic properties and structure of Fe₂O₄ films before and after annealing at various temperatures.

2. Experimental Procedure

Fe₂O₄ films were prepared at room temperature (RT) by ion beam sputtering from a Fe₂O₄ target on Si (111) substrates covered with a 10-nm-thick SiO₂ buffer layer. All films were covered with an 1-nm-thick SiO₂ layer as a capping layer in order to prevent oxidation. The base pressure of the apparatus was better than 1.0 × 10⁻⁴ Pa, and the argon pressure during sputtering was 0.02 Pa. The acceleration voltage of the ion gun was 1200 V with the ion current of 120 mA. The deposition rates for Fe₂O₄ films and SiO₂ layers were 0.11 nm/s and 0.12 nm/s, respectively. The thickness of the Fe₂O₄ films was fixed at 100 nm. The as-deposited Fe₂O₄ films were annealed at the temperature (Tₐ) in the range of 573–973 K for 1h, in a vacuum with pressure better than 1.3 × 10⁻⁴ Pa.

The magnetization curves of the Fe₂O₄ films were measured using a vibrating sample magnetometer (VSM) with a maximum field of 794 kA/m at RT. The magnetic field for the measurement was applied parallel to the film plane. The structure of the Fe₂O₄ films was characterized by an X-ray diffractometer (XRD) with Cu-Kα radiation and a transmission electron microscope (TEM). The chemical state in the Fe₂O₄ films was identified and determined by an X-ray photoelectron spectroscopy (XPS) with Al-Kα radiation.

3. Results and Discussion

Figure 1 shows magnetization curves of 100-nm-thick Fe₂O₄ films before and after annealing at various temper-
Fig. 1 Magnetization curves of 100-nm-thick Fe$_3$O$_4$ films before and after annealing at various temperatures ($T_a$). The magnetic field was applied parallel to the film plane.

Fig. 2 Saturation magnetization ($M_s$) and coercivity ($H_c$) in the 100-nm-thick Fe$_3$O$_4$ film as a function of annealing temperature ($T_a$). Empty circles (○) and solid circles (●) show $M_s$ and $H_c$, respectively.

At each $T_a$, a hysteresis loop is observed apparently. Its shape changes markedly as $T_a$ increases. In order to investigate the marked change in the loop in detail, the saturation magnetization, $M_s$, and the coercivity, $H_c$, were summarized in Fig. 2 as a function of annealing temperature, $T_a$, for the 100-nm-thick Fe$_3$O$_4$ films. $M_s$ increases markedly up to $T_a = 573$ K; increases gradually in the region of $T_a = 573$–873 K, and slightly decreases above $T_a = 873$ K. Each $M_s$ value is lower than that of the bulk Fe$_3$O$_4$ (0.598 Wb·m$^{-2}$).$^{13}$ $H_c$ also increases up to $T_a = 873$ K, and then slightly decreases above $T_a = 873$ K. These results are considered to be due to that the structures of the film, which includes the phase and the grain size, changes with increasing $T_a$.

In order to explore the origin of the change of magnetic properties in Fe$_3$O$_4$ films with annealing temperature, we determined the chemical state in these films by XPS measurements. Figure 3 shows Fe 2p core-level XPS spectra in the 100-nm-thick Fe$_3$O$_4$ films before and after annealing at various temperatures, $T_a$. The broad peak is observed around 712 eV at each $T_a$, which corresponds to Fe$_3$O$_4$ spectra reported by Y. X. Lu et al.$^{27}$ These broad Fe 2p3/2 peaks are attributed to the coexistence of Fe$^{3+}$ and Fe$^{2+}$. The satellite peak cannot be almost observed around 719 eV at all $T_a$. These results mean that the possibility of the existence of the Fe$_2$O$_3$ phase in our films is low before and after annealing. On the basis of these results, it is considered that the chemical state in these films is mainly close to that of the Fe$_3$O$_4$ phase.

In order to clarify the change of the structure in Fe$_3$O$_4$ films with annealing temperature in more detail, we performed XRD measurements of these films. Figure 4 shows high-angle XRD profiles of 100-nm-thick Fe$_3$O$_4$ films before and after annealing at various temperatures, $T_a$. In every case, the peak originating from the Si substrate is confirmed at around $2\theta = 42.8^\circ$. The peak which corresponds to Fe$_3$O$_4$ (222) is observed at around $2\theta = 37.2^\circ$ above $T_a = 573$ K, and becomes sharp as $T_a$ increases. This means that the grain size of Fe$_3$O$_4$ increases with increasing $T_a$. The broad peak appears approximately at $2\theta = 36.2^\circ$ above $T_a = 673$ K, which is derived from Fe$_3$O$_4$ (311). Additionally, as shown by an arrow, above $T_a = 873$ K, the peak clearly appears at around $2\theta = 39.0^\circ$, which originates from α-Fe$_2$O$_3$ (222).
These peak positions shift to higher angles than those of bulk Fe3O4 and α-Fe2O3. These peak shifts are attributed to the tensile stress in the film plane. Thus, it can be considered that a polycrystalline Fe3O4 phase is mainly formed in the film and its grain size increases up to \( T_a = 873 \) K, and that not only the Fe3O4 phase but also the α-Fe2O3 mixed phase is formed in the film above \( T_a = 873 \) K.

In order to verify this change of the phase in the film with annealing, we carried out TEM observations of Fe3O4 films. Here, as an example, the selected area diffraction (SAD) patterns of 100-nm-thick Fe3O4 films before and after annealing at \( T_a = 873 \) K are shown in Fig. 5. In the film before annealing [Fig. 5(a)], many diffraction rings caused by the Fe3O4 phase are observed. Additionally, the weak diffraction ring is observed between Fe3O4 (400) and (422), which might be derived from the secondary phase such as the γ-Fe2O3 phase. This reveals that the polycrystalline Fe3O4 phase is mainly predominant in the film before annealing. This is also considered that the secondary phase such as the γ-Fe2O3 phase is slightly included in the film before annealing. On the other hand, in the film after annealing at \( T_a = 873 \) K [Fig. 5(b)], in addition to many diffraction rings originating from the Fe3O4 phase, several other diffraction rings can be observed. Their rings are caused by α-Fe2O3 (012), (202), (024), (122), (214) and (300). This means that the Fe3O4 and α-Fe2O3 phases, which are polycrystalline, coexist in the film after annealing at \( T_a = 873 \) K. The Fe3O4 and α-Fe2O3 mixed phases are formed in the Fe3O4 mixed phases (0 ≤ x ≤ 0.5), as can be seen in the phase diagram of an Fe-O system.29) On the basis of these results, it can be verified that the polycrystalline Fe3O4 phase mainly exists in the film at all \( T_a \). It can also be found that the α-Fe2O3 phase is formed above \( T_a = 873 \) K. Note that no rings corresponding to any other possible phase, such as Fe and FeO, are observed in any film at all \( T_a \). As a consequence, it is found that the annealing effect on magnetic properties and structure in the Fe3O4 film are correlated each other; the change of magnetic properties in the film below \( T_a = 873 \) K are mainly caused by the increase of the grain size in the Fe3O4 phase with annealing, and the change of magnetic properties in the films above \( T_a = 873 \) K is due to that the α-Fe2O3 phase is apparently formed in the film at \( T_a = 873 \) K.

4. Conclusions

The change of the magnetic properties and structure in Fe3O4 films on Si substrates with the annealing temperature, \( T_a \), has been studied in detail. As to magnetic properties in the Fe3O4 films, the saturation magnetization and the coercivity markedly increase with increasing \( T_a \) up to 873 K, and then slightly decrease above \( T_a = 873 \) K. As to structure in the Fe3O4 films, Fe3O4 phase is mainly predominant in the film.
up to $T_a = 873$ K, and its grain size increases with increasing $T_a$. The Fe$_3$O$_4$ phase and the $\alpha$-Fe$_2$O$_3$ phase coexist above $T_a = 873$ K. On the basis of these results, it is concluded that the change of magnetic properties in the Fe$_3$O$_4$ film up to $T_a = 873$ K are attributed to the growth of Fe$_3$O$_4$ phase, namely, the increase of the grain size in the Fe$_3$O$_4$, and the change of magnetic properties above $T_a = 873$ K are influenced by the formation of $\alpha$-Fe$_2$O$_3$ phase.

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