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Influence of reducing thermo-chemical treatment on magnetic properties of magnetite Fe_3O_4 (1 0 0) epitaxial films

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Abstract

The effect of low temperature annealing in a reducing atmosphere on the magnetic properties of epitaxial magnetite (1 0 0) films grown on MgO (1 0 0) substrate was investigated. We found that the magnetization of the films increases and the coercivity decreases with treatment in CO at the partial pressure of 1.01×10^5 Pa at 250 °C. The annealed films show a sharp Verwey transition. Marginal change in the stoichiometry of the films is not the reason for the magnetization enhancement. It is thought that the decrease of antiphase boundaries density and the oxygen vacancies produced at the antiphase boundaries are responsible for the observed results.

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Keywords: Magnetization; Magnetite; Antiphase boundaries; Annealing effect

Magnetite (Fe_3O_4) is a half-metallic ferrimagnet and as a result it currently attracts a lot of interest from the spin electronics community. In practice, epitaxial magnetite films grown on MgO substrate are known to always have antiphase boundaries (APBs) adversely affecting their magnetic properties [1–3]. Due to frustrated exchange interaction established across APBs, the saturation magnetization of the films is reduced and their coercivity is increased. As a result the potential for applications of magnetite films in spin electronic devices is hampered. To enhance the magnetization of the films, especially under a low magnetic field, we attempted to post-treat the magnetite epitaxial films under different atmospheres. It was recently reported by us that the magnetization of epitaxial magnetite films grown on MgO (1 0 0) substrate remarkably increases (15%) and the coercivity decreases after just 4 min of mild annealing in an oxidizing atmosphere (250 °C) that leaves the film stoichiometry essentially unchanged [4]. In situ resistance measurements during the annealing reveal that the oxidation at APBs occurs much faster than in the domains neighbouring the APBs. It is thought that the change in the stoichiometry of the APBs is responsible for the enhancement of the magnetization of the films at the early stage of the oxidation. A model is proposed that involves the decay of the antiferromagnetic coupling and frustrated exchange interaction associated with the change in the stoichiometry at APBs [5].

In this study we decided to anneal the sample in reducing atmosphere. The aim was to have the annealing conditions mild enough so that the stoichiometry of the film is not altered, like in our recent studies. We followed the same logic expecting that the changes should be localized in the vicinity of APBs. The intent was to study the effect of the stoichiometry change at the APBs on the magnetization of the films. In other words we aimed to

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extract the influence of the APBs stoichiometry change on exchange frustration caused by the APBs.

We used epitaxial magnetite films with a thickness of 100 nm grown on MgO (0 0 1) single crystal substrates. The films were grown by oxygen-plasma-assisted molecular beam epitaxy. The substrate temperature during the growth was 250 °C which is as high as the annealing temperature. Other details of the film growth are reported in Ref. [4]. Several techniques including in situ reflection high-energy electron diffraction (RHEED), high-resolution X-ray diffraction (HRXRD), alternating gradient force magnetometer (AGFM), Raman spectroscopy (RS), high-resolution transmission electron microscopy (HRTEM), Mössbauer spectroscopy and resistivity measurements were employed to characterize the epitaxial magnetite (Fe_3O_4) films. All of the results indicate the films were of a high quality. The films were annealed at 250 °C under 1.01×10^5 Pa reducing atmosphere (carbon monoxide). HRXRD was employed to evaluate the strain status of the annealed films. Hysteresis loop measurements were carried out using a MicroMag 3900 AGFM at room temperature. To avoid the error introduced by the distribution of film thickness and volume among different film specimens, a single specimen was employed for magnetic measurements before and after the annealing treatment. The four-probe method was employed for the resistance measurements.

The (0 0 4) symmetric and (2 2 6) asymmetric rocking curves of the as-grown and annealed films are shown in Fig. 1. The out-of-plane and in-plane lattice parameters of the as-grown film as calculated from the HRXRD results were 8.3716 and 8.4264 Å, respectively. The in-plane lattice parameter of the film is exactly twice that of the MgO substrate implying that the film is fully strained on the MgO substrate. The diffraction peaks of the annealed film shift marginally to the higher angle side. From the separation of the substrate and the annealed film, the out-of-plane and in-plane lattice parameter of the annealed film were calculated as 8.3670 and 8.4262 Å, respectively. The in-plane lattice parameter of the annealed film is the same as that of the as-grown film implying that the annealed film still remains in a fully strained state.

It is known that the Verwey transition temperature (T_v) of magnetite is very sensitive to the stoichiometry. The Verwey transition is suppressed even by small deviations from stoichiometry [6]. Thus, the change in the T_v could be used to evaluate the change in the stoichiometry of the films after annealing. The resistance vs. temperature (R–T) curves of as-grown and annealed films are shown in Fig. 2. It is found that, even after 30 min of annealing, the films still show a clear Verwey transition which is evaluated from the jump of the film resistance on the R–T curve. T_v of as-grown and 30 min annealed film is 113 and 101 K, respectively. A sharper transition is observed for the annealed film which implies that the annealed film has a higher uniformity. The existence of a Verwey transition suggests that the stoichiometry of the annealed films remains close to that of ideal magnetite. One can therefore arrive at the conclusion: annealing in CO does not significantly change the stoichiometry of the film (less than 1.2%).

The hysteresis loops of the as-grown and annealed films are shown in Figs. 3a and b. One can see from Fig. 3a that, compared to the as-grown films, the annealed films are easier to saturate and show a higher magnetization at a given field. The magnetization under 796 kA/m, increases by 7% and 12% for films annealed at 30 and 60 min, respectively, compared to that of the as-grown film. Fig. 3b shows the hysteresis loops and virgin magnetization curve of the as-grown and annealed films in a low magnetic field. Meanwhile, the coercivity of the annealed films decreases following the

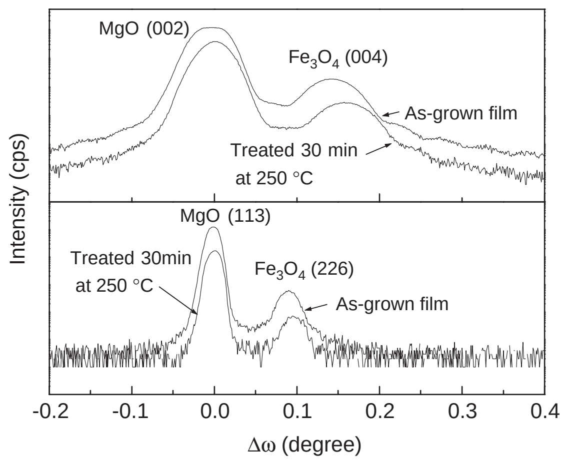

Fig. 1. Rocking curve of the magnetite film for symmetric (0 0 4) and asymmetric (2 2 6) diffraction before and after treatment.

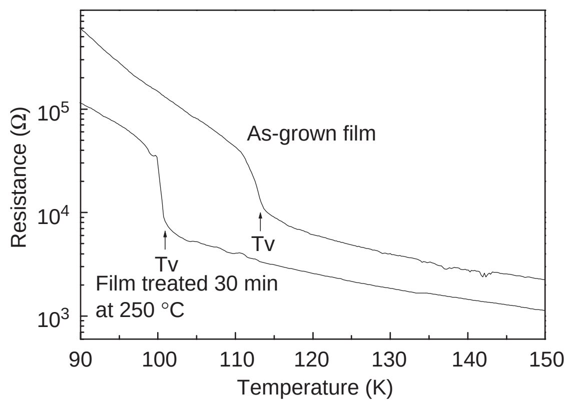

Fig. 2. Resistances of the as-grown and annealed magnetite films vs. temperature.