Magnetic Properties of Spinel Ferrite Thin Films Grown by Reactive Sputtering

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We report the crystal structure and magnetic properties of spinel ferrite thin films of magnetite, maghemite, and cobalt ferrite grown by reactive magnetron sputtering. The magnetic properties of spinel ferrite films, in particular saturation magnetization, are affected by the growth conditions, even when no significant difference is found in the crystal structures. Comparing films grown by molecular beam epitaxy with those produced by reactive magnetron sputtering, we found that the latter technique produces larger saturation magnetization than the bulk. Therefore, sputtering can be considered the suitable method for preparing various spinel ferrite compounds. [doi:10.2320/matertrans.ME201504]

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1. Introduction

For modern applications of magnetism and spintronics, thin-film growth of functional magnetic materials is one of the key technologies. Even if a fascinating magnetic material is experimentally found or theoretically proposed, it cannot be used for application unless appropriate growth technique is established. Since some of the spinel ferrites exhibit relatively large magnetization and a much higher Curie temperature as compared to room temperature, they have been utilized in various magnetic devices as well as recording technology. For example, magnetite (Fe3O4) is believed to be half-metallic; cobalt and nickel ferrites are promising insulators used as tunneling barriers in a spin filter device; epitaxially distorted cobalt ferrite thin films possess high magnetic anisotropy and are potentially useful in magnetic recording media unaccompanied by platinum group elements or rare earth elements.

Magnetite is composed of only two elements, iron and oxygen, and is a prototype spinel ferrite. Epitaxial thin films of magnetite can be prepared by different methods such as molecular beam epitaxy (MBE) with oxidation sources, pulse laser deposition (PLD) in an oxygen atmosphere, magnetron sputtering, and so on. For industrial-scale production, a physical vapor deposition (PVD) method, such as the sputtering process, for high-throughput synthesis is desirable.

Since physical characterization of thin films with a complicated crystal structure like spinel cannot be achieved as easily as that for bulk materials, it is also difficult to define the criteria of film quality for every compound. In the case of magnetite films, the nature of the metal-insulator transition known as the Verwey transition is suitable for evaluating film quality. We can expect a high-quality film to exhibit a Verwey temperature as high as that observed for bulk and resistivity at the Verwey temperature should show an increase of 2–3 orders of magnitude. The resistivity at room temperature, which is quite easy to determine, can also be a useful measure of film quality. Whatever the growth technique of the magnetite films, relatively high quality films can be obtained if the growth conditions are sufficiently optimized.

In the case of thin films of other spinel ferrites like cobalt and nickel ferrite, defining film quality is slightly difficult as they are inherently insulators and no unique characteristic physical property seems to exist. Unlike the magnetite thin films, reported cobalt-ferrite thin films frequently exhibit significantly less magnetization than the bulk. In addition, most magnetization processes of these spinel ferrite films are quite complicated suggesting that various magnetic inhomogeneities are incorporated. This is a potentially serious problem for advanced spintronic uses. Recently, we have found that high quality epitaxial films of these spinel ferrites can be grown by reactive magnetron sputtering techniques and that epitaxial distortion causes the ferrite film to exhibit high magnetic anisotropy.

In this paper, we present an overview of the developed film growth technique based on a reactive sputtering method and the magnetic and structural properties of the as-grown epitaxial thin films magnetite, maghemite, and cobalt-ferrite. In the following section, the experimental procedures for growing spinel ferrite films are described. The third section introduces results and discussion regarding the magnetism of the particular spinel ferrites magnetite, maghemite, and cobalt ferrite. The fourth section presents the summary.

2. Experiment

In order to obtain oxide films via the sputtering method, there are two options regarding the sputtering targets. One is using a sintered oxide compound with the desired composition, while the other is using a metal target in the presence of the reactive gas oxygen. To grow films of iron oxides such as Fe2O3 and γ-Fe2O3, different types of targets were used in our study: hematite (α-Fe2O3), wüstite (FeO) and iron metal (α-Fe)57.

For cobalt ferrite film growth, Fe-Co alloy targets of different compositions were selected. All the sputtering processes were carried out by using the reactive radio frequency (RF) sputtering technique with a mixture of Ar and O2 gas. MgO(001) single crystals were used as substrates. The oxygen flow rate and temperature were the growth parameters.

A typical growth condition was as follows. 30 sccm of Ar...
gas was introduced, and oxygen flow rate ($\varphi_{O_2}$) was controlled. The total gas pressure was around 0.5 Pa. The RF sputtering power was 100 W. Single crystal MgO (001) was used as the substrate. After the substrate was heated at 400–600°C for 15 min or longer, pre-sputtering was performed for 10 min in 30 sccm Ar gas flow. Successively, sputtering deposition was carried out. After deposition, reflection high energy electron diffraction (RHEED) measurements were performed.

3. Results and Discussion

3.1 Iron oxide film

Figure 1 shows typical RHEED images of ferrite ($\text{Fe}_3\text{O}_4$) thin films on MgO(001) sputtered using a pure iron target under different $\varphi_{O_2}$ conditions. The RHEED images of the film surfaces (Figs. 1(b)–(d)) show a clear streak, indicating a high-quality film with regards to crystallinity.

A summary of the various physical properties such as saturation magnetization, resistivity, composition ratio of Fe$^{3+}$ and Fe$^{2+}$ evaluated by Mössbauer experiment and film growth rate as a function of oxygen flow rate is given in Fig. 2. A strong correlation between resistivity and Fe$^{3+}$ composition ratio can be observed. The resistivity of the films grown at $\varphi_{O_2}$ between 0.7 to 1.7 sccm is close to that of magnetite. Temperature dependence of these films exhibits clear Verwey transition at around 110 K, indicating that the film is of high quality. In addition, films grown under even higher oxygen flow exhibit saturation magnetization comparable to that of either magnetite or maghemite. All of the experimental information indicates that Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ were selectively grown on MgO(001) substrates by simply changing $\varphi_{O_2}$ using reactive sputtering with a metal Fe target.

Iron flux rate also abruptly changes in the transition region between Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ film growth, suggesting that the growth mode affects the film grown. Metal mode sputtering produces Fe$_3$O$_4$ of a less oxide state and oxide mode creates $\gamma$-Fe$_2$O$_3$. We also discovered similar selective growth of Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ with FeO target. Interestingly, Fe$_3$O$_4$ was produced without oxygen while $\gamma$-Fe$_2$O$_3$ was created when oxygen was introduced.

At present, the relation between the sputtering mode and the oxidation state of the grown Fe$_3$O$_4$ films is not clear. In order to reveal the growth and oxidation mechanism, direct observation of the Fe target surface and analysis of the oxidation state are required. We note that the magnetic properties as well as the crystal structures of our magnetite films are comparable to those previously reported films grown by other deposition techniques$^{13}$.

![Fig. 1 RHEED images of sputtered Fe oxide films. Images of (a) MgO substrate, (b) $\alpha$-Fe grown without $O_2$ flow, (c) Fe$_3$O$_4$ grown with $\varphi_{O_2}$ of 1.0 sccm and (d) $\gamma$-Fe$_2$O$_3$ grown with $\varphi_{O_2}$ of 4.0 sccm are shown. (after ref. 17).](image)

![Fig. 2 O$_2$ dependence of the various sputtered iron-oxide films. (a) Dependence of growth rate, (b) saturation magnetization ($M$) at room temperature, (c) room-temperature resistivity, (d) Mössbauer intensity ratio of Fe$^{3+}$ to total Fe for the iron-oxide films, and (e) effective iron flux estimated from (a) and the densities of Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ (after ref. 17).](image)
3.2 Cobalt ferrite film

Fe$_{1-x}$O$_x$ films with acceptable magnetic properties can be grown by MBE, PLD and sputtering techniques; however, thin films of other spinel ferrites seem to be strongly dependent on the growth techniques and growth conditions. Saturating magnetization of previously reported cobalt-ferrite (CFO) films grown by MBE techniques is much smaller than that of bulk, even though the diffraction patterns are visually excellent. The bulk value of CFO is 425 emu/cm$^3$, while our MBE-grown CFO films and also others gave a value of only 320 emu/cm$^3$ or less\(^8\). The main reason behind the greatly reduced saturation magnetization is believed to be the existence of anti-phase boundaries (APBs).

Recently, we found that CFO films grown on MgO(001) substrates by reactive sputtering exhibit large saturation magnetization comparable to the bulk and extremely high uniaxial magnetic anisotropy of 13 Merg/cm$^3$ along the normal to the film.\(^5\) The composition ratio of Fe and Co is also a crucial parameter.\(^6\) Assuming that the A-sites are fully occupied by 3+ cations and the B-sites are occupied by an equal number of 2+ and 3+ cations, the composition of the film can be described by Co$_x$Fe$_{3-x}$O$_4$. As $x$ increases to 1 which corresponds to a stoichiometric cobalt ferrite compound, both the saturation magnetization and the squareness of the MH loop decrease significantly. We note that different $x$ requires different optimal oxygen flow rate and process temperature.

Figure 3 shows MH-loops of CFO(001) films grown on MgO(001) with thickness of 60 nm for $x = 0.75$ at different growth temperatures. Magnetic field was applied along the perpendicular to the film plane. All of the MH-loops indicate that the preferential magnetization direction is normal to the film. One can see that the substrate temperature is also an important key to growing high-quality CFO films. The shape of the hysteresis loop is affected by substrate temperature. A higher growth temperature causes larger saturation magnetization and produces more square-shaped MH loops. By taking into account both saturation magnetization and squareness, the growth temperature of 600°C can be considered optimal for this composition.

Composition dependence of the uniaxial anisotropy obtained at room temperature for different $x$ is shown in Fig. 4. Although the growth conditions for all samples with different $x$ have not been optimized as yet, it is observed that $K_u$ increases with Co concentration to 15 Merg/cm$^3$. Since the origin of high $K_u$ in this system is Co$^{2+}$ ions located at the spinel’s B-sites in a tetragonally distorted crystal field,\(^{19,20}\) the monotonic increase of $K_u$ with $x$ is qualitatively understood. Extraplated curve of $K_u$ at $x \rightarrow 0$ does not seem to go through the origin, suggesting the mechanism of $K_u$ in pure magnetite or maghemite ($x = 0$) is not fully understood as yet. Although the direction and amplitude of the Co$^{2+}$ occupied B-site distortion mainly determine the value of $K_u$,\(^{19,20}\) quantitative understanding is needed to control $K_u$.

4. Summary

We showed experimentally that the reactive magnetron sputtering technique is suitable for growing epitaxial thin films of magnetite, maghemite and cobalt ferrite. Although other physical vapor deposition techniques can grow structurally good epitaxial films of cobalt ferrite, magnetic qualities of those films are much poorer than those grown by reactive sputtering. Especially, the saturation magnetization in films grown by the sputtering method are as large as that of the bulk. Details of the growth conditions during reactive sputtering of spinel ferrite films containing the multi-valence element Fe must be understood to improve film quality and for application in advanced spintronic materials.

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