Large Faraday effect in a short wavelength range for disordered zinc ferrite thin films

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We have prepared a zinc ferrite (ZnF_2O_4) thin film 85 nm thick deposited on a silica glass substrate by using a radio frequency sputtering method. Faraday effect measurements have been carried out not only for as-deposited but also for annealed thin films. The thin film annealed at 300 °C as well as the as-deposited thin film exhibit a large Faraday rotation angle at a wavelength of around 390 nm. In particular, the thin film annealed at 300 °C manifests the largest Faraday effect among the present thin films; the rotation angle of 1.65°/μm is attained at a wavelength of 386 nm. The thin films 1.08 μm thick exhibit a large magnetization at room temperature, and the dependence of the magnetization on the external magnetic field is suggestive of a ferrimagnetic behavior. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2199727]

The stable phase of zinc ferrite ($ZnFe_2O_4$) possesses a normal spinel structure, in which antiferromagnetic order results due to Fe^{3+} ions in octahedral sites (B sites) below about 10 K, i.e., Néel temperature. But a nonzero magnetization can be observed at room temperature when $ZnFe_2O_4$ is quickly cooled from elevated sintering temperatures. In particular, an unusually large magnetization is observed at room temperature for a superfine particle of $ZnFe_2O_4$,[1–8] a rapidly quenched $ZnFe_2O_4$,[9–11] and a gas phase-derived thin film of $ZnFe_2O_4$.[12–15] The large magnetization is attributable to such a structure that a site exchange between Zn^{2+} in the A site (tetrahedral site) and Fe^{3+} in the B site takes place, and that the strong superexchange interaction between Fe^{3+} ions in A and B sites leads to a ferrimagnetic order at least for localized magnetic moments even above the room temperature. We recently reported that the $ZnFe_2O_4$ thin film prepared by a sputtering method manifests a large magnetization of 32 emu/g at room temperature and a large Faraday effect in a wavelength range of 450–500 nm.[13] Considering the application of magneto-optical materials for laser diodes operating at a blue to a near ultraviolet region, it is very important to obtain information about the Faraday effect at a wavelength range shorter than 400 nm or so. In the present investigation, we report on the large Faraday effect of the $ZnFe_2O_4$ thin film derived by the sputtering method in a shorter wavelength region such as 350–400 nm. We also demonstrate that annealing at relatively low temperatures such as 300 °C for $ZnFe_2O_4$ thin film enhances the Faraday rotation angle at a wavelength of around 400 nm.

$ZnFe_2O_4$ thin films were prepared by using a radio frequency (rf) sputtering method (ULVAC RFS-200). ZnO and Fe_2O_3 (hematite) powders were weighed so that the molar fractions of ZnO and Fe_2O_3 were equivalent to each other and mixed thoroughly. The mixture was compacted into a mould made of copper and was used as a target. The sputtering was carried out for 2 or 24 h under conditions that the rf power was 150 W, the atmosphere was a mixture of 20% O_2 and 80% Ar, and the gas pressure was 1.5×10^{-2} Torr. $ZnFe_2O_4$ was deposited on a silica glass plate as a substrate heated at 200 °C. The as-deposited thin films were annealed at elevated temperatures for 3 h in air. The thickness of the thin films was measured by using a surface roughness meter (KLA Tencor, ASIQ).

The as-deposited and annealed thin films were subjected to an x-ray diffraction analysis with a Cu K_α radiation (Rigaku RINT2500) to ascertain that the thin film is composed of a single phase of $ZnFe_2O_4$. The microstructure of the thin film was observed by means of transmission electron microscopy (TEM) with Philips CM200 at 200 kV. Optical absorption spectra were obtained for the thin films at room temperature using a spectrophotometer (JASCO, V-570). A variation of the Faraday rotation angle with a wavelength was explored by using a commercially available measurement system for Faraday and Kerr effects (JASCO, Model K-250). A dc magnetic field of 1.5 T, the direction of which was perpendicular to the film surface, was applied. The measurements were performed at room temperature. Magnetization as a function of external magnetic field was measured at 300 and 5 K by using a superconducting quantum interference device magnetometer (Quantum Design, MPMS2). The magnetic field was varied from −5 to 5 T.

Figure 1 shows the magnetization as a function of the external magnetic field at 5 and 300 K for the as-deposited and annealed $ZnFe_2O_4$ thin films 1.08 μm thick. The annealing was carried out at 300 °C. The magnetization of the as-deposited $ZnFe_2O_4$ thin film is 23 emu/g at 300 K when the external magnetic field is 5 T. This value is somewhat smaller than that reported previously.[13] This is because the sputtering conditions such as kinds of glass substrate, atmosphere during sputtering, gas pressure, rf output power, and so forth are different. A similar phenomenon that magnetic properties such as magnetization are very sensitive to the preparation conditions was reported for $ZnFe_2O_4$ thin films prepared by pulsed laser deposition.[12] The large magnetization at 300 K is imposed to the site exchange between Zn^{2+}

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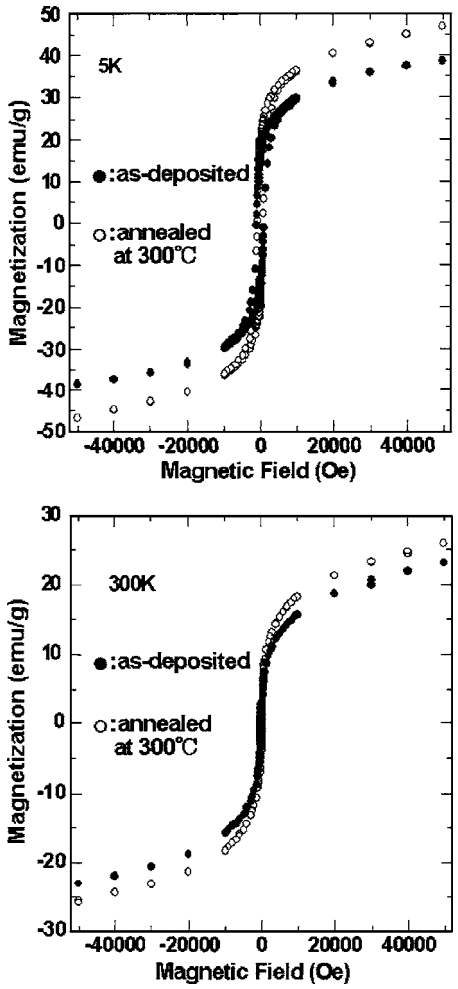

FIG. 1. Dependence of magnetization on external magnetic field at 5 and 300 K for as-deposited (closed circles) and annealed (open circles) $ZnFe_2O_4$ thin films prepared by the sputtering method. The annealing temperature is 300 °C.

ions in A sites and Fe^{3+} ions in B sites, as described above.

It is found in Fig. 1 that the magnetization of the $ZnFe_2O_4$ thin film annealed at 300 °C is larger compared with the as-deposited thin film at both 5 and 300 K; the values of magnetization at 5 T are 39 and 47 emu/g for as-deposited and annealed thin films, respectively, when the temperature is 5 K. Although the reason why the annealing at 300 °C enhances the magnetization of the sputtered $ZnFe_2O_4$ thin film still remains open, we suggest a couple of possibilities. Figure 2 depicts a plane view TEM image of the as-deposited $ZnFe_2O_4$ thin film. The micrograph seems to indicate that the thin film is composed of concentrated crystalline nanoparticles dispersed in an amorphous matrix. The diameter of the crystalline particles is about 8–15 nm, coincident with the value estimated from x-ray diffraction lines, i.e., 5 nm or so.[14] The presence of an amorphous phase formed via a rapid quenching process provided by the sputtering is a main reason why the present $ZnFe_2O_4$ thin film exhibits magnetization somewhat smaller than the value previously reported. Furthermore, it is speculated that $ZnFe_2O_4$ crystals in which Fe^{3+} and Zn^{2+} ions are randomly distributed are precipitated in the amorphous phase by the annealing at 300 °C; the volume fraction of the crystalline phase is increased by the annealing. Thus, the possible precipitation of $ZnFe_2O_4$ crystalline phases, which possess a large magnetization due to the disordered distribution of Fe^{3+} and Zn^{2+} ions, in the amorphous phase may lead to the enhancement of the magnetization caused by the annealing at 300 °C. Another possibility is the variation of the distribution of Fe^{3+} ions in the spinel structure of $ZnFe_2O_4$ nanoparticles with the annealing at 300 °C. The magnetization of $ZnFe_2O_4$ strongly depends on the deviation in the site occupation from the normal spinel structure. A fraction of Fe^{3+} ions which occupy the A sites has a great influence on the resultant magnetization.

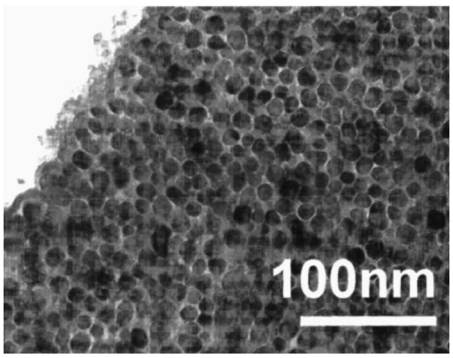

FIG. 2. Plane view TEM image taken from as-deposited $ZnFe_2O_4$ thin film.

As reported previously, the sputtered $ZnFe_2O_4$ thin films exhibit a magnetic transition like those of cluster spin glasses.[15] We have preliminarily confirmed that the present thin films manifest similar features. Namely, the magnetic susceptibility takes a maximum at a certain temperature in the temperature dependence of susceptibility when the zero-field cooling is carried out. By contrast, the susceptibility increases monotonically with a decrease in temperature when the field cooling is performed. Such a cluster spin glasslike behavior partly stems from the disordered distribution of Fe^{3+} and Zn^{2+} ions in the spinel structure of $ZnFe_2O_4$. In such a structure, magnetic clusters composed of Fe^{3+} ions are present and bring about the cluster spin glasslike transition. Namely, a superparamagnetic blocking of the clusters accompanied with intercluser interactions takes place. In addition, the nanoparticles of which the thin film is composed, as shown in Fig. 2, can contribute to the superparamagnetic blocking as well. At the transition, the magnetic interaction among the nanoparticles plays an important role because the nanoparticles are present so closely to each other. Thus, magnetic properties such as cluster spin glasslike transition and large magnetization at room temperature are soundly explained in terms of the disordered distribution of Fe^{3+} ions over the A and B sites in the spinel structure as well as the microstructure of the thin film. The cationic distribution may be estimated from mutual zero-field and in-field low temperature Mössbauer measurements.

Figure 3 illustrates optical absorption spectra for $ZnFe_2O_4$ thin films 85 nm thick. The spectra for the as-deposited thin film and those after annealing at 300 and 800 °C are shown. All the spectra manifest an intense absorption in a wavelength range shorter than about 500 nm; an absorption peak is clearly observed at about 310 nm. The absorption coefficient at around 310 nm is smaller for an-

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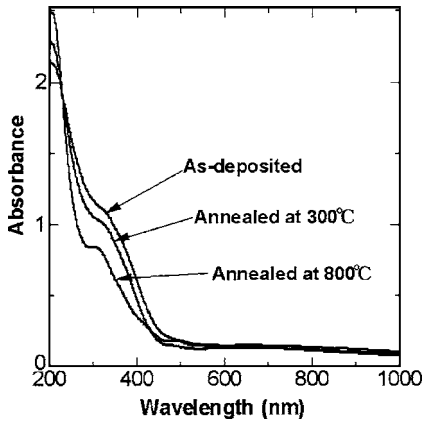

FIG. 3. Optical absorption spectra for as-deposited and annealed $ZnFe_2O_4$ thin films. The annealing temperature is 300 and 800 °C.

nealed thin films than for the as-deposited film and is apt to decrease gradually as the annealing temperature increases. Considering that $MgFe_2O_4$ and $LiFe_5O_8$ exhibit an optical absorption band starting at 2 eV, which is assigned to the $d \rightarrow s$ transition,[16] and a similarity in the crystal structure between those ferrites and $ZnFe_2O_4$, we can speculate that the absorption in a wavelength range from 300 to 400 nm is attributed to the $3d^5 \rightarrow 3d^4 4s^1$ transition of Fe^{3+} ions, where the $4s$ orbital of Fe^{3+} is thought to contribute to the conduction band.

In Fig. 4 is shown the variation of the Faraday rotation angle with wavelength for as-deposited and annealed $ZnFe_2O_4$ thin films. The Faraday effect is evidently observed for the as-deposited thin film and those heat treated at 300 and 400 °C. By contrast, the Faraday rotation angle is very small for the thin film annealed at 800 °C. The absolute value of the Faraday rotation angle manifests its maximum at around 380–390 nm. The maximum of the absolute value of the Faraday rotation angle for the as-deposited thin film is $1.37°/\mu m$ at the wavelength of 386 nm. The Faraday effect is enhanced for the thin films after annealing at 300 °C; the maximum absolute value of the Faraday rotation angle is $1.65°/\mu m$ at 386 nm for the thin film annealed at 300 °C. Recently, Faraday rotation angles for $Co_{0.5}Fe_{2.5}O_4$ (Ref. 17) and $Co_{0.85}Zn_{0.15}Fe_2O_4$ (Ref. 18) thin films were reported, but the measurements were restricted within a wavelength range longer than 475 nm. Considering the optical absorption spectra shown in Fig. 3, the Faraday effect illustrated in Fig. 4 is attributable to the $3d^5 \rightarrow 3d^4 4s^1$ transition of Fe^{3+} ions. In addition, the fact that the Faraday rotation angle is enhanced by the annealing at 300 °C is coincident with the enhancement of the magnetization by the annealing at 300 °C shown in Fig. 1. Besides, the disappearance of the Faraday rotation for the thin film annealed at 800 °C is explainable in terms of the change of the crystal structure with annealing. The annealing of the thin film at high temperatures such as 800 °C is apt to bring about the formation of $ZnFe_2O_4$ with the normal spinel structure, leading to the very small Faraday rotation angle as well as a small magnetization.

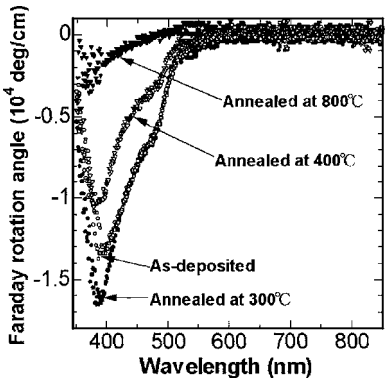

FIG. 4. Faraday rotation angle as a function of wavelength for as-deposited (open circles) and annealed $ZnFe_2O_4$ thin films. The annealing temperature is 300 (closed circles), 400 (open triangles) and 800 °C (closed triangles).

In conclusion, we found that large Faraday effect takes place in a short wavelength range such as 390 nm for $ZnFe_2O_4$ thin films prepared by the sputtering method. In particular, the thin film annealed at relatively low temperatures such as 300 °C as well as the as-deposited film exhibit a large Faraday rotation angle; the thin film annealed at 300 °C manifests the maximum rotation angle of $1.65°/\mu m$ at a wavelength of 386 nm.

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