MAGNETO-OPTICAL PROPERTIES OF COMPOSITE FILMS OF MAGNETITE FINE PARTICLES SOLIDIFIED BY POLYVINYL ALCOHOL

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Abstract—Magneto-optical properties of composite films of magnetite fine particles solidified by polyvinyl alcohol (PVA) were investigated. The films were formed by spin-coating a mixed solution of magnetite colloidal suspension and PVA dissolved in distilled water on glass substrates and dried at various temperatures from room temperature to 200 °C. With elevating drying temperature, the Faraday rotation $\theta_F$ decreases, and the optical transmittance, conversely, increases. The $\theta_F$-spectrum varies in a manner that $\theta_F$ increases with wavelength in the visible region, takes a maximum at about 700 nm and decreases with wavelength in the near infrared region. The films in which magnetite particles are aligned in chain clusters along the film thickness, were prepared by applying a dc magnetic field during drying process. We observed the anisotropy of $\theta_F$ in these films.

KEYWORDS: FARADAY EFFECT, FINE PARTICLES, COMPOSITE MATERIALS, MAGNETITE

INTRODUCTION

Associated with the rapid progress of laser and other optoelectronic technology, the development of high quality magneto-optical materials is an urgent problem. The material requirements for light control devices are large magneto-optical effect and high optical transmittance. In this respect, iron-garnets such as YIG and BIG have been actively investigated in many laboratories. We also reported magnetic and magneto-optical properties of Bi-substituted YIG films synthesized by sol-gel method [1]. Besides this, we have investigated composite materials consisting of ferromagnetic fine particles solidified by transparent materials. When the size of the particles is much smaller than the wavelength of light, even metals with large optical absorption can be used if fine particles of the materials are dispersed in transparent solids. Therefore, it is expected to develop new magneto-optical materials according to this guiding principle. However very few investigations have been made on magneto-optical effects of such discontinuous materials [2]. Previously we prepared films consisting of magnetite [$Fe_3O_4$] fine particles of a water-based magnetite ferrofluid, solidified by PVA (polyvinyl alcohol), and successfully produced films with magnetic and optical anisotropies. The films are composed of magnetite chain clusters aligned by the solidification in an applied magnetic field [3]. In this study, we investigated magneto-optical effect of the films for light transmitted through the film (Faraday effect).

EXPERIMENT

PVA was dissolved in a water-based magnetite ferrofluid (Matsumoto Oil & Chemicals, Co.) which was diluted with distilled water to control the viscosity of the solution. The size of magnetite particles is about 100 Å in average diameter. The solution with an appropriate viscosity was coated onto glass substrates by spin-on technique. Then coated films were dried in air at various temperatures from 25 °C up to 200 °C. The volume fraction of magnetite particles in the films, $f$, was estimated from the ratio of magnetization in film (measured at 15 kOe) to the saturation magnetization in magnetite (Ms=471 G) [4]. The film thickness was restricted to be about 20 μm by a single spin-coating to prevent the film peeling off from the substrate. In this way, good-quality films having a flat surface and no cracks were successfully fabricated.

RESULTS AND DISCUSSION

Figure 1 shows typical examples of Faraday hysteresis loops of a film dried at room temperature measured at two different wavelengths of $\lambda=470$ nm and 800 nm. These loops are characterized by small coercive force and large saturation field. This is evidence that magnetite particles are fine and are isolated from one another by PVA, thus magnetic properties of the films are superparamagnetic.

Figure 2 shows the Faraday rotation $\theta_F$ spectra of films of $f=7.2\%$, for the drying temperature as a parameter. The shapes of the spectra are almost similar irrespective of drying temperature; $\theta_F$ increases in the visible region, takes a
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**Fig. 1** Faraday hysteresis loops at \( \lambda = 470 \) and \( 800 \) nm of films with \( f = 4.0\% \).

**Fig. 2** The dependence of Faraday rotation \( \theta_f \) at \( 8\) kOe on wavelength, where the films with \( f = 7.2\% \) were dried at various temperatures.

**Fig. 3** The dependence of Faraday rotation \( \theta_f \) at \( \lambda = 633\) nm and saturation magnetization \( M_s \) on drying temperature.

**Fig. 4** X-ray diffraction patterns (Cu:K\( \alpha \)) of films with \( f = 7.2\% \) dried at room temperature, 120°C and 200°C.

maximum around 700 nm and then gradually decreases with wavelength in the near infrared region. The magnitude of \( \theta_f \), is, on the contrary, subject to a drastic decrease by elevating drying temperature. The wavelength at which \( \theta_f \) takes maximum and the wavelength at which the sign of \( \theta_f \) is reversed are subject to shift to longer wavelength with raising drying temperature. The drying temperature dependence of \( \theta_f \) (films of \( f = 7.2\% \)) is plotted for a fixed wavelength of \( \lambda = 633\) nm in Fig. 3, together with the dependence of saturation magnetization \( M_s \). It is suggested from the figure that \( \theta_f \) and \( M_s \) are closely correlated phenomena. The reduction of \( M_s \) may be attributed to the progression of oxidation of magnetite particles by raising drying temperature. This inference can be confirmed by measuring film structure by X-ray diffraction (Cu:K\( \alpha \)). The result is shown in Fig. 4. All diffraction lines are ascribed to those from magnetite, but a slight decrease of diffraction intensity is observed as drying temperature was raised, indicating that magnetite particles in the films are in part oxidized, but this is insufficient to explain the reduction of \( \theta_f \). Thus we supposed that the surface of magnetite particles was oxidized, which may lead to a large reduction of \( \theta_f \) as observed in Figs. 2 and 3, because the Faraday effect of particle in a dispersed medium is predominantly determined by the surface portion of the particles.

We are interested in magneto-optical effect of such composite materials with magnetic particles dispersed in a non-magnetic transparent matrix. Unfortunately, there have been few investigations on the Faraday effect in such discrete media. To begin with, we examined the dependence of \( \theta_f \) (at \( \lambda = 633\) nm) on the volume fraction of magnetite particles \( f \) for films dried at room temperature as shown in Fig. 5. A linear relationship between \( \theta_f \) and \( f \) holds. By extrapolating the line to \( f = 100\% \) (i.e. the genuine magnetite film), \( \theta_f \) is estimated to be \( 1.11 \times 10^4 \)

Fig. 5 The dependence of Faraday rotation $\theta_F$ at 633nm on the volume fraction $f$. (deg/cm), which is the same order in magnitude of $\theta_F=3.9\times10^4$(deg/cm) of magnetite film [5].

Figure 6 is the variation of $\theta_F$-spectrum against film thickness for the samples of $f=4.0$% dried at room temperature. The shape of $\theta_F$-spectrum, except for its magnitude, is nearly kept unchanged regardless of film thickness in the wavelength region $\lambda\geq550$nm, while a noticeable change in the thickness dependence of $\theta_F$ is recognized in the wavelength region $450$nm$\leq\lambda\leq550$nm, where $\theta_F$ is negative and a sharp peak appears, which shifts to longer wavelength with increasing film thickness. This situation is shown in Fig. 7 for several wavelengths. A linear relationship between Faraday rotation and film thickness holds for $\lambda\leq550$nm, while Faraday rotation varies in an extraordinary way with film thickness for $450$nm$<\lambda<550$nm. This may be due to the fact that the magneto-optical interaction is influenced strongly by the spacing of particles in this wavelength region.

Fig. 7 The dependence of Faraday rotation $\theta_F$ of films ($f=4.0$%) on film thickness for several wavelengths.

Magnetooptical materials used in light control devices must have high transmittance. Figure 8 shows the transmittance of films ($f=7.2$%) dried at various temperatures. Quite different from the Faraday rotation, the transmittance increases with drying temperature, that is, the Faraday rotation and the transmittance are in trade-off relation with respect to drying temperature. The quality of magneto-optical materials are usually evaluated by the figure of merit, $\theta_F/a$ ($a$ is the absorption coefficient). Figure 9 is the dependence of figure of merit of films dried at various temperatures on wavelength. The figure of merit becomes larger with lowering the drying temperature and its maximum value is obtained at a wavelength near 750nm unless the drying temperature exceeds 180°C.

Fig. 8 The dependence of transmittance of films ($f=7.2$%) on drying temperature.

All films referred so far were prepared in the absence of a magnetic field during drying the coated solution, where magnetite particles are considered to be randomly dispersed in PVA. Next, we will consider the effect of applying a magnetic field during drying on
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Fig. 9 The dependence of figure of merit at 8kOe on wavelength, where the films (\(f=7.2\%\)) were dried at various temperatures.

MAGNETO-OPTICAL EFFECT. It is expected that the film structure changes by formation of chain clusters of magnetite particles aligned along the magnetic field [3]. In this experiment, a dc magnetic field \(H_d\) up to 10 kOe was applied perpendicular to the substrate plane. Figure 10 is Faraday hysteresis loops at \(\lambda=633\text{nm}\) for films \((f=4.1\%)\) solidified in (a) \(H_d=0\) and (b) 1kOe. A significant difference in hysteresis loop by \(H_d\) appears in the region of small field strength; the slope of the curve (b) is steeper than that of the curve (a). The variation of the initial susceptibility of \(\theta_F\), i.e., \(\chi=(3\theta_F/3H)H=0\), is attributed to the anisotropy introduced by \(H_d\). Figure 11 shows the dependence of Faraday rotation \(\theta_F\) at \(\lambda=633\text{nm}\) on \(H_d\) for two different measurement fields of 1 kOe and 8 kOe. \(\theta_F\) at 1 kOe increases rapidly until \(H_d\) reaches at 1 kOe and then decreases very slowly with increasing \(H_d\). The initial rapid increase in \(\theta_F\) is interpreted by the formation of chain clusters of magnetite particles. On the other hand, \(\theta_F\) at 8kOe decreases monotonously and very slowly with increasing \(H_d\). The slow decrease of \(\theta_F\) in large \(H_d\) may be attributed to the progression of particle aggregations, which rather acts as destruction of chain cluster configuration. Solidification of the solution in a magnetic field is preferable to construction of actual magneto-optical devices because the initial susceptibility of \(\theta_F\) increases by the formation of chain clusters of magnetite particles.

In conclusion, we reported magneto-optical properties of composite films of magnetite fine particles dispersed in PVA. Besides this, we are now examining another combination of composite materials of cobalt fine particles dispersed in a transparent polymer and found that Faraday effect of this material is quite different from that of cobalt itself, which will be reported elsewhere.

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