Magnetic and optical properties of MgAl$_2$O$_4$-(Ni$_{0.5}$Zn$_{0.5}$)Fe$_2$O$_4$ thin films prepared by pulsed laser deposition

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Abstract

Thin films composed of MgAl$_2$O$_4$ and (Ni$_{0.5}$Zn$_{0.5}$)Fe$_2$O$_4$ ([MA($100-x$)-NZFx] films) were grown on fused SiO$_2$ substrates by pulsed laser deposition. X-ray diffraction measurements revealed that the films were polycrystalline, and that their lattice constant varied linearly with composition, indicating the formation of a solid solution. The film with $x = 60$ was paramagnetic and those with $x \geq 70$ were ferromagnetic. The films had a transparency above 75% in the visible range, but the transparency decreased with the $x$ value. The optical band gaps were 2.95, 2.55, 2.30 and 1.89 eV for $x = 20, 40, 60$ and 100, respectively. The Faraday rotation angle increased with $x$ in the visible range, and the film with $x = 70$ exhibited a value of 2000 degrees cm$^{-1}$ at 570 nm, which is comparable to the rotation angle of Y$_3$Fe$_5$O$_{12}$. Owing to their high transparency, which extends into the visible range, the [MA($100-x$)-NZFx] films can be used in novel magneto-optical devices.

Keywords: transparent magnetic thin film, solid solution of nickel zinc ferrite and magnesium aluminum spinel, Faraday rotation angle, pulsed laser deposition (PLD)

1. Introduction

The magneto-optical properties of ferrites have been attracting considerable attention because of their possible application to magneto-optical recording [1-4], optical isolators [5, 6] and optical circulators [7]. Yttrium iron garnet (YIG) is used for Faraday rotation devices in the wavelength range of 1.3–1.5 $\mu$m because this material exhibits high transparency in the range of 1–8 $\mu$m [8] and a large Faraday rotation angle [9]. Therefore, YIG is a technologically important magnetic material for use in optical isolators. However, YIG has low transparency at wavelengths shorter than 1 $\mu$m [8]. The requirements for the next-generation Faraday rotation device are transparency and appreciable Faraday rotation angle in the visible light range. These requirements urge the development of new magnetic materials.

In this study, we examined spinel-type ferrites, which are ternary compounds with a cubic symmetry and a general formula of M$_x$Fe$_{3-x}$O$_4$, where M denotes a divalent metal cation. Compounds containing an element in two different oxidation states, such as spinel-type ferrites, often have strong absorption in the visible light range, which can be attributed to intervalence charge-transfer transitions [10]. Therefore, the Faraday rotation angle is larger in spinel-type ferrites than in garnet-type ferrites such as YIG. This property is advantageous for the miniaturization of optical isolators because the same Faraday rotation angle can be achieved with a thinner film. A spinel-type ferrite with high transparency
in the visible range can be used in optical communication devices such as optical isolators. In this study, we examined a novel transparent spinel-type ferrite with a large Faraday rotation angle. The ferrite is based on the solid solution of (Ni, Zn)Fe$_2$O$_4$ (NZF) and MgAl$_2$O$_4$ (MA), which we label as [MA(100 − x)]-NZF$_x$. Here, NZF is ferromagnetic and is known as a promising ferrite with high magnetization [11, 12], whereas MA is paramagnetic and is transparent in the visible range [13]. Both NZF and MA have a cubic spinel structure and their lattice parameters are very similar (NZF: 0.8370 nm and MA: 0.8083 nm); therefore, these compounds are expected to form a solid solution. In this paper, we report the magnetic and optical properties and Faraday rotation of [MA(100 − x)]-NZF$_x$ thin films prepared by pulsed laser deposition (PLD).

2. Experimental details

The [MA(100 − x)]-NZF$_x$ thin films were deposited from ceramic targets that were synthesized using a conventional solid-state reaction as follows. Reagent-grade MgO, Al$_2$O$_3$, NiO, ZnO and Fe$_2$O$_3$ powders were mixed and calcined at 800 °C for 2 h. After calcination, the [MA(100 − x)]-NZF$_x$ powders were ground, pressed into pellets, and sintered at 1350 °C for 4 h. The pellets were irradiated with a focused KrF excimer laser, at a repetition rate of 7 Hz, fluence of approximately 2 J cm$^{-2}$, and an under oxygen pressure of 10 mTorr at 600 °C, to deposit 180-nm-thick films on fused SiO$_2$ substrates. To maintain the same thickness, the cross section of the films was observed using scanning electron microscopy (SEM) and the results were fed back to the deposition. The crystal phases were identified using x-ray diffraction measurements (XRD, D8 Advance; Bruker AXS, Germany). The surface morphology and roughness of the films were characterized with an atomic force microscope (AFM, SPI3800N; SII NanoTechnology Inc., Japan). The film composition was measured with an x-ray fluorescence spectrometer (XRF, MP4 with FP Multi; PANalytical, Netherlands), which was calibrated using standard samples. Magnetic hysteresis loops were measured at room temperature using a vibrating sample magnetometer (VSM, BHV-35; Riken Denshi, Japan) in a magnetic field of up to 10 kOe. Optical transmittance spectra were recorded with a UV–Vis spectrophotometer (UV-3150; Shimadzu Corp., Japan), and the Faraday rotation spectra were measured using a polarization-modulation-type spectrometer (K-250; Jasco Inc., Japan), at room temperature in a magnetic field of 4 kOe. The polarization and wave vector of the linearly polarized incident light were parallel and normal to the film plane, respectively.

3. Results and discussion

Figure 1 shows XRD patterns of [MA(100 − x)]-NZF$_x$ films. They reveal a polycrystalline cubic spinel with a poor crystallinity. The broad band at 22° corresponds to the fused SiO$_2$ substrate; it partly masks the 111 reflection of spinel at 18°. XRF measurements revealed that all the films have a stoichiometric composition. Figure 2 shows the variation of the lattice constant with x. These lattice constants of pure MA (x = 0) and NZF (x = 100) thin films are very close to the corresponding bulk values, and the lattice constant increases linearly with x between these extremes. From Vegard’s law, this behavior proves the formation of a solid solution. The AFM images of the films (figure 3) show a smooth surface with an rms roughness of ∼1 nm and a grain size of ∼30 nm for any composition. Figure 4 shows the M–H curves of the [MA(100 − x)]-NZF$_x$ thin films. This figure reveals that the film with x = 60 is paramagnetic and the films with higher x values are ferrimagnetic. The saturation magnetization of pure NZF decreases markedly with increasing MA content in [MA(100 − x)]-NZF$_x$ films, suggesting that the substitution of MA for NZF reduces the superexchange interaction. The saturation magnetization of the NZF (x = 100) film is about twice smaller than the bulk NZF value (400 emu cm$^{-3}$). This decrease can be attributed to the low crystallinity of the film, the presence of oxygen vacancies and anti-phase boundaries [14]; however, it is unclear which factor is dominant.
Figure 3. AFM images of the [MA(100 − x)-NZFx] thin films for x = 100 (a), 80 (b), 60 (c), 40 (d), and 20 (e).

![AFM images](image)

Figure 4. M–H curves of the [MA(100 − x)-NZFx] thin films measured at room temperature.

![M–H curves](image)

Figure 5. UV–Vis spectra of the [MA(100 − x)-NZFx] thin films for x = 100 (a), 80 (b), 60 (c), 40 (d), and 20 (e).

![UV–Vis spectra](image)

The UV–Vis transmittance spectra shown in figure 5 reveal a high transparency of above 75% for all the [MA(100 − x)-NZFx] thin films. The transparency decreases and the absorption edge shifts to longer wavelength with increasing x. The optical band gap was evaluated from the slope of the graph of $(\alpha h\nu)^{2/3}$ versus the photon energy $h\nu$ [15], where $h$ and $\nu$ denote the Planck’s constant and frequency, respectively. The absorption coefficient $\alpha$ was calculated as

$$\alpha = \frac{\ln((1-R)/T)}{t},$$

where $T$, $R$ and $t$ are the transmittance, reflectance and film thickness, respectively [16]. From figure 6, the optical band gap was deduced as 2.95, 2.55, 2.30, 2.05 and 1.89 eV for x = 20, 40, 60, 80 and 100, respectively. The value for the NZF film (1.89 eV for x = 100) is larger than that of bulk NZF (1.66 eV) [17], which can be attributed to nonstoichiometry, low crystallinity and residual stress. Indeed, Kozhevnikov et al reported that the band gap of strontium ferrite (SrFeO$_y$) is sensitive to nonstoichiometry [18]. Chen et al documented changes in the band gap of Zn$_{1-x}$Cd$_x$O thin film deposited by dc reactive sputtering with the full-width at half-maximum of the (002) XRD peak [19]. They found that the film with a lower crystallinity has a wider band gap and this tendency agrees well with our results. Zhao et al reported that the band gap energy of GaN thin film deposited by metal organic chemical vapor deposition (MOCVD) changes with in-plane stress [20]. To assess the possible nonstoichiometry, we tried to measure the electrical conductivity of the [MA(100 − x)-NZFx] thin films using a dc four-probe method, but the resistivity was higher than the measurement limit. We also sought to measure the residual stress in the film using the x-ray sin$^2$Ψ method, but because of the low crystallinity, it...
was difficult to evaluate the stress. The optical band gap of bulk MA is 7.80 eV [21]. Therefore, the observed band gap decrease with the $x$ value agrees with the fact that the band gap is narrower for NZF than for MA.

Figure 7 shows optical absorption spectra of the [MA(100 $- x$)]-NZF $x$ thin films. An absorption threshold is seen at approximately 600 nm, which results from the transitions between the crystal-field split levels of Ni$^{2+}$ [22]. A feature at approximately 500 nm corresponds to the intervalence charge transfer from Fe$^{2+}$ to Fe$^{3+}$ [22]. Another threshold appearing at 400 nm can be assigned to the 3d$^5$ $\rightarrow$ 3d$^4$4s$^1$ transition in ZnFe$_2$O$_4$ [23].

Figure 8 shows the wavelength dependence of the Faraday rotation angle for the [MA(100 $- x$)]-NZF $x$ thin films. The Faraday rotation angle increases with the $x$ value at any wavelength in the measured spectral range. There are two distinct peaks at approximately 500 and 550 nm; they correspond to the absorption features in figure 7 and therefore can be attributed to the same mechanisms. The film with $x = 70$ has a Faraday rotation angle of 2000 degrees cm$^{-1}$ at a wavelength of 570 nm, which is comparable to the rotation angle of YIG [6]. This film is ferromagnetic and has a high transmittance; it therefore might find magneto-optical applications in the visible spectral range.

### 4. Conclusions

In an attempt to develop a novel magneto-optical material, we have prepared a series of solid-solution thin films composed of MgAl$_2$O$_4$ and (Ni$_{0.5}$Zn$_{0.5}$)Fe$_2$O$_4$ by PLD on a fused SiO$_2$ substrate. We found that the magnetic properties, optical band gap, transmittance and Faraday rotation angle can be controlled by changing the $x$ value in the [MA(100 $- x$)]-NZF $x$ composition. The film with $x = 70$ had a Faraday rotation angle of 2000 degrees cm$^{-1}$ at a wavelength of 570 nm, which is comparable to the rotation angle of Y$_3$Fe$_5$O$_{12}$. The [MA(100 $- x$)]-NZF $x$ thin films have high transparency extending into the visible range and therefore can be used in novel magneto-optical devices.

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