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Preparation and Faraday effect of EuS microcrystal-embedded oxide thin films

Katsuhsa Tanaka\textsuperscript{a)}
Department of Chemistry and Materials Technology, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606-8585, Japan

Naoki Tatehata, Koji Fujita, and Kazuyuki Hirao
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshidahommachi, Sakyo-ku, Kyoto 606-8501, Japan

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EuS microcrystal-embedded SiO$_2$, Al$_2$O$_3$, and TiO$_2$ thin films have been prepared by using rf sputtering method. X-ray diffraction analysis indicates that EuS microcrystal is precipitated as a single phase in Al$_2$O$_3$ and TiO$_2$ films while precipitation of EuS is not detected in SiO$_2$ film. Faraday effect attributable to the $4f^7-4f^65d$ transition of Eu$^{2+}$ in EuS microcrystalline phase is observed in Al$_2$O$_3$ and TiO$_2$ films. In particular, Faraday rotation angle observed for EuS-embedded TiO$_2$ film is large; for instance, the magnitude of Verdet constant for as-deposited TiO$_2$ film prepared without heating of substrate during the sputtering is 0.15 deg/cm Oe at wavelength of 700 nm. This value is larger by two orders of magnitude than those of Eu$^{2+}$- or Tb$^{3+}$-containing oxide glasses which show the largest Faraday rotation angle among rare-earth-containing glasses, and is comparable to the value for EuSe single crystal. © 2001 American Institute of Physics.

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I. INTRODUCTION

The Faraday effect is applicable to many devices in the field of optoelectronics such as an optical isolator, an optical switch, an optical circulator, an optical memory, and so forth. Recent advancement in fabrication of laser diodes with a wavelength corresponding to visible to ultraviolet range requires a Faraday rotator which works efficiently in such a wavelength region. One candidate for that purpose is inorganic glass containing a large amount of rare-earth ions. As indicated by many researchers,\textsuperscript{1–15} rare-earth-containing oxide and fluoride glasses exhibit Faraday rotation in the visible region. The magnitude of Faraday rotation angle increases monotonically with a decrease in the wavelength, and this relationship is described well in terms of the single oscillation model derived from a theory of Van Vleck and Hebb\textsuperscript{16} for a paramagnetic solid. As argued by Shafer and Suits,\textsuperscript{3} the Faraday rotation angle of rare-earth-containing glasses is determined by probability and wavelength of $4f-5d$ transitions as well as magnetic susceptibility of each rare-earth ion. Since the magnetic susceptibility of glass depends on the content of rare-earth ion and the transition wavelength is significantly affected by ligand field strength around a rare-earth ion, the Faraday rotation angle at a discretion-ary wavelength can be readily changed by varying the glass composition.\textsuperscript{13,14} Nonetheless, the Verdet constant, i.e., Faraday rotation angle per unit length of light path and unit external magnetic field, is not so large compared with ferromagnetic or ferrimagnetic materials like rare-earth iron garnets.\textsuperscript{17–19} This is because the superexchange interaction among rare-earth ions in glasses is generally very small; the rare-earth-containing glass shows paramagnetism even at very low temperatures like 1 K or so.\textsuperscript{4}

Another promising material applicable to Faraday effect devices in the visible range is a semimagnetic semiconductor such as (Cd,Mn)Te.\textsuperscript{20,21} It is known that a large Zeeman splitting in semimagnetic semiconductors leads to a large Faraday effect. For instance, Cd$_{0.2}$.Mn$_{0.8}$.Te thin film prepared by the ionized-cluster beam method exhibits a Verdet constant of about $-0.2$ deg/cm Oe, which brings about magneto-optical figure of merit larger than 45 deg/dB that is required for practical application to an optical isolator, when the wavelength is longer than about 650 nm.\textsuperscript{22} Additional effect to enhance the Faraday rotation angle is possibly realized when the microcrystals of semimagnetic semiconductor are embedded in a transparent thin film. Because the quantum confinement effect in a microcrystalline semiconductor leads to an increase of oscillator strength, the enhancement of Faraday effect may be caused by the increased oscillator strength of microcrystals in such a composite material.\textsuperscript{23} In addition, the dielectric constant of matrix in the composite inevitably has influence on the Faraday rotation angle obtained for the composite material.\textsuperscript{24} Several studies have been done concerning the magneto-optical properties of composite thin films in which microcrystalline semimagnetic semiconductors as well as metals are embedded.\textsuperscript{25–27} In the case of semimagnetic semiconductor-embedded thin films, the wavelength dependence of the Faraday rotation angle manifests a blue-shift due to the quantum size effect.\textsuperscript{27} EuS is one of the semimagnetic semiconductors, and possesses a variety of interesting magnetic properties. Although stoichiometric EuS exhibits transition between ferromagnetic and paramagnetic phases at 16.6 K, incorporation

\textsuperscript{a}Electronic mail: katsu@ipc.kit.ac.jp
of trivalent rare-earth ions such as Gd$^{3+}$ into EuS brings about a drastic increase of Curie temperature because the number density of magnetic polarons is increased by the doping of trivalent rare-earth ions.$^{28}$ Also, addition of SrS into EuS leads to a spin glass phase.$^{29}$ The magneto-optical properties of EuS were measured as well, and the variation of Faraday rotation angle with wavelength was analyzed in terms of the electronic structure of EuS.$^{30-32}$ To our knowledge, however, magneto-optical properties of EuS microcrys-

tals embedded in dielectric thin films have not been reported. In the present investigation, we report successful preparation of EuS microcrystal-embedded oxide thin films by means of an rf sputtering method. We show that in particular, EuS-embedded TiO$_2$ films exhibit a large Faraday effect.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

EuS microcrystal-embedded oxide thin films were prepared by using an rf sputtering method. SiO$_2$, Al$_2$O$_3$, and TiO$_2$ were used as a matrix of the composite film. Bulk SiO$_2$ glass, sintered Al$_2$O$_3$, and sintered TiO$_2$ were used as sputtering targets. Seven pieces of EuS pellets, prepared by pressing EuS powder under a hydrostatic pressure of about 20 MPa, were placed on the target material. The area fraction of EuS pellets on the oxide target was about 47%. The sputtering was carried out under a flow of Ar gas. The gas pressure was 1.0 $\times$ 10$^{-2}$ Torr. The rf output power was 100 W.

Commercially available AF45 glass (non-alkali borosilicate glass) was used as a substrate. The substrate was heated at 200 °C, or not heated; two ways were adopted for the treatment of substrate. The deposition time was 25 h. Some of the thin films thus obtained were heat-treated at 450 °C in an Ar atmosphere.

B. Measurements

X-ray diffraction analysis with Cu $K_\alpha$ radiation was performed for as-deposited and heat-treated samples to identify crystalline phases if precipitated. EuS powder, a raw material for preparation of composite films, was also subjected to the measurement of Faraday and Kerr effects (JASCO, Model K-250) utilized for the measurements. A Xe lamp was used as the light source. The wavelength was varied from 850 to 400 nm. The external magnetic field was fixed to be 15 kOe. The Verdet constant of the thin films was calculated from the Faraday rotation angle, magnetic field, and thickness of the film. The Faraday rotation angle of the thin film was estimated by subtracting the Faraday rotation angle of the substrate from that of the film with the substrate. The thickness of the thin films was estimated from scanning electron micrographs of the samples.

III. RESULTS

X-ray diffraction patterns, of as-deposited and heat-
treated thin films prepared by heating the substrate at 200 °C, are shown in Figs. 1(a) and 1(b), respectively. The x-ray diffraction pattern of EuS powder is also depicted in each of the figures. Precipitation of EuS is observable in both as-deposited and heat-treated Al$_2$O$_3$ and TiO$_2$ thin films. The intensity of the diffraction line corresponding to the main peak of EuS is higher in the TiO$_2$ than in the Al$_2$O$_3$ films. In contrast, diffraction lines ascribable to EuS are not observed in as-deposited and heat-treated SiO$_2$ films. Figures 2(a) and 2(b) show the x-ray diffraction patterns of as-deposited and heat-treated thin films for which the substrate was not heated during the sputtering. Precipitation of EuS is evident in the as-deposited Al$_2$O$_3$ and TiO$_2$ thin films, while EuS is not precipitated in either as-deposited or heat-treated
SiO$_2$ films. The EuS phase is also crystallized in heat-treated Al$_2$O$_3$ film. In the case of heat-treated TiO$_2$ film, an x-ray diffraction pattern could not be obtained because some parts of the film were peeled by the heat treatment. Broad diffraction lines due to EuS are observed in the patterns of Al$_2$O$_3$ and TiO$_2$ films as shown in Figs. 1 and 2. This suggests that the crystallite size of the EuS precipitated in these films is very small. The results derived from the x-ray diffraction analysis clearly indicate that Al$_2$O$_3$ and TiO$_2$ are suitable as the matrix material for EuS microcrystalline phase-embedded composite thin films whereas the SiO$_2$ is not fit for that purpose. A similar result was reported for Cd,Mn$_2$Te microcrystal-embedded dielectric films. When an attempt was made to prepare the film by using SiO$_2$ as the matrix, (Cd,Mn)$_2$Te was barely precipitated because of the oxidation of Mn$^{2+}$. Although the (Cd,Mn)$_2$Te microcrystalline-embedded SiO$_2$ films were successfully prepared by Nasu et al., the volume fraction of (Cd,Mn)$_2$Te microcrystalline phase was so small as 4 vol %.

Room temperature $^{151}$Eu Mössbauer spectra of the as-deposited SiO$_2$, Al$_2$O$_3$, and TiO$_2$ films are shown in Fig. 3. The absorption bands centered at around IS = 0 mm/s and -12 mm/s, where IS represents the isomer shift, are ascribable to Eu$^{3+}$ and Eu$^{2+}$ ions, respectively. The absorption area ratio of Eu$^{2+}$ to Eu$^{3+}$ was estimated by fitting Lorentzian curves to the experimental data. The results are summarized in Table I. As pointed out in previous studies, the absorption area ratio is not equal to the molar ratio of Eu$^{2+}$ to Eu$^{3+}$ because the temperature dependence of recoilless fraction is different between Eu$^{2+}$ and Eu$^{3+}$. Since the Debye temperature for the chemical bond relevant to Eu$^{2+}$ is lower than that concerning Eu$^{3+}$, the molar fraction of Eu$^{2+}$ in the total number of europium ions is more than the value listed in Table I. Table I indicates that the molar fraction of Eu$^{2+}$ is the largest for the TiO$_2$ films and the smallest for the SiO$_2$ films. In other words, most of the Eu$^{2+}$ ions were oxidized during the sputtering when SiO$_2$ was used as the target. This is a phenomenon similar to the oxidation of Mn$^{2+}$ observed for the (Cd,Mn)$_2$Te-embedded SiO$_2$ film described above.

Variation of the Verdet constant with wavelength is shown for SiO$_2$ films in Fig. 4. Figures 4(a) and 4(b) correspond to the SiO$_2$ thin films prepared with and without heating of the substrate, respectively. In both Figs. 4(a) and 4(b), dotted and solid lines denote as-deposited and heat-treated SiO$_2$ films, respectively. The Verdet constant $V$ was evalu-

| Table I. Absorption area fraction of Eu$^{2+}$ and Eu$^{3+}$ in $^{151}$Eu Mössbauer spectra for as-deposited SiO$_2$, Al$_2$O$_3$, and TiO$_2$ thin films containing EuS. |
|-----------------|-----------------|-----------------|
| Matrix          | Substrate temperature (°C) | Eu$^{2+}$ | Eu$^{3+}$ |
| SiO$_2$         | 200, not heated    | 3          | 97        |
|                 | 200, heated        | 0          | 100       |
| Al$_2$O$_3$     | 200, not heated    | 14         | 86        |
|                 | 200, heated        | 20         | 80        |
| TiO$_2$         | 200, not heated    | 22         | 78        |
|                 | 200, heated        | 40         | 60        |
The Faraday rotation angle due to the diamagnetism of substrate glass was subtracted from the experimental value to obtain the Faraday rotation angle caused by the thin film. The Verdet constant is negative and decreases monotonically with a decrease in wavelength for the SiO₂ films prepared with the substrate temperature being 200 °C [Fig. 4(a)]. A similar tendency is observed for the SiO₂ film prepared without heating of the substrate as far as the wavelength range longer than 500 nm is concerned [Fig. 4(b)].

The dependence of the Verdet constant on wavelength is shown for EuS microcrystal-embedded Al₂O₃ and TiO₂ thin films in Figs. 5 and 6, respectively. In these figures, (a) and (b) represent the Verdet constants of thin films prepared with and without heating of substrate during the sputtering, respectively, and dotted and solid lines denote as-deposited and heat-treated films, respectively. The wavelength dispersion of the Verdet constant shown in these figures manifests a similar tendency to each other; the Verdet constant shows a maximum and a minimum at around 550–600 and 650–700 nm, respectively. The behavior of the Verdet constant shown in Figs. 5 and 6 is coincident with the wavelength dispersion of the Verdet constant for EuS crystal reported previously.30,31 In other words, the Faraday effect of the present EuS microcrystal-doped Al₂O₃ and TiO₂ thin films is unambiguously brought about by the EuS microcrystalline phases. The Verdet constant of EuS-containing SiO₂, Al₂O₃, and TiO₂ thin films at a wavelength of 700 nm is summarized in Table II. Verdet constants of rare-earth-containing glasses are also shown in the table. The magnitude of the Verdet constant for as-deposited TiO₂ thin film prepared without the heating of the substrate during the sputtering is 0.15 deg/cm Oe, which is larger by two orders of magnitude than those of rare-earth-containing glasses. Also, this value is comparable to the magnitude of the Verdet constant for EuSe single crystal (0.18 deg/cm Oe at 633 nm and 0.16 deg/cm Oe at 666 nm).35,36

\[
\theta = VHI. \quad (1)
\]

The Faraday rotation angle \( \theta \) of sample thickness \( l \) and external magnetic field \( H \) using the following relation:

\[
\theta = VHI.
\]
The results of x-ray diffraction analyses and Mössbauer effect measurements clearly indicate that TiO$_2$ is the most suitable as the host material for the EuS-embedded thin film among the present three kinds of oxides, whereas SiO$_2$ is not appropriate for that purpose. It is speculated that the great glass-forming ability of SiO$_2$ makes the precipitation of crystalline phases difficult, leading to the amorphous films as shown in Figs. 1 and 2. The wavelength dependence of the Verdet constant at a wavelength range longer than 500 nm for SiO$_2$ films shown in Fig. 4 manifests a tendency similar to those observed for rare-earth-containing glasses; the Verdet constant is negative and the magnitude of the Verdet constant increases with a decrease in wavelength. This tendency is describable in terms of the single oscillator model within the framework of the theory of Van Vleck and Hebb:

\[
V^{-1} = \frac{g \mu_B \hbar}{4 \pi^2 \chi C_c} \left( 1 - \frac{\lambda^2}{\lambda_t^2} \right),
\]

where \(\chi\) is the magnetic susceptibility, \(g\) is the Landé factor, \(\mu_B\) is the Bohr magneton, \(c\) is the velocity of light, \(h\) is the Planck constant, \(\lambda\) is the wavelength of incident light, \(\lambda_t\) is the effective transition wavelength, and \(C_c\) is the effective transition probability. The relationship between the magnitude of the inverse Verdet constant and the square wavelength is shown for the present SiO$_2$ films in Fig. 7. Open circles, closed circles, and open squares in Fig. 7 denote the as-deposited film prepared by heating the substrate, its heat-treated sample, and as-deposited film prepared without heating of the substrate, respectively. The solid lines were drawn by the least squares method.

**TABLE II.** Verdet constant at 700 nm for SiO$_2$, Al$_2$O$_3$, and TiO$_2$ thin films containing EuS. Verdet constants for rare-earth-containing glasses are also shown for comparison. (RT is room temperature.)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Substrate temperature (°C)</th>
<th>Verdet constant (deg/Oe cm) as-deposited</th>
<th>Verdet constant (deg/Oe cm) heat-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>200</td>
<td>(-2.4 \times 10^{-4})</td>
<td>(-2.1 \times 10^{-3})</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>(-7.8 \times 10^{-3})</td>
<td>(-7.8 \times 10^{-3})</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>200</td>
<td>(-7.9 \times 10^{-3})</td>
<td>(-0.011)</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>(-0.041)</td>
<td>(-0.035)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>200</td>
<td>(-0.091)</td>
<td>(-0.10)</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>(-0.15)</td>
<td></td>
</tr>
<tr>
<td>25 Th$_2$O$_3$–75 P$_2$O$_5$ glass</td>
<td></td>
<td>(-2.5 \times 10^{-3})</td>
<td></td>
</tr>
<tr>
<td>34 EuO·15 Al$_2$O$_3$·51 B$_2$O$_3$ glass</td>
<td></td>
<td>(-4.5 \times 10^{-3})</td>
<td></td>
</tr>
</tbody>
</table>
angle and dielectric constant of the dispersed phase and matrix. In the case that magnetic spheres with a dielectric tensor written as 

$$\epsilon = \begin{pmatrix} \epsilon & i\gamma & 0 \\ -i\gamma & \epsilon & 0 \\ 0 & 0 & \epsilon \end{pmatrix}$$  \hspace{1cm} (3)$$

are embedded in a matrix with a dielectric constant of $\epsilon_1$, the diagonal and off-diagonal elements of the dielectric tensor, $\epsilon_{xx}$ and $\epsilon_{xy}$, for the composite is expressed as follows: \cite{24}

$$\epsilon_{xx} = \epsilon_1 + \frac{3f\epsilon_1(e - \epsilon_1)}{3\epsilon_1 + (1-f)(e - \epsilon_1)}$$  \hspace{1cm} (4)$$

$$\epsilon_{xy} = \frac{3if\epsilon_1\gamma}{3\epsilon_1 + (1-f)(e - \epsilon_1)}$$  \hspace{1cm} (5)$$

where $f$ is the volume fraction of the dispersed spheres. The Faraday rotation angle $\Theta$ and the ellipticity angle $\Psi$ of the composite material is written as follows:

$$\Theta - i\Psi = -i(\pi/\lambda)\epsilon_{xy}/\epsilon_{xx}^{1/2}.$$  \hspace{1cm} (6)$$

The effect of $\epsilon_1$, the dielectric constant of the matrix, on the Faraday rotation angle of composite material is complicated as indicated by Eqs. (4)–(6), although an increase of $\epsilon_1$ increases the magnitude of imaginary part of $\epsilon_{xy}$ when both $\epsilon_1$ and $\epsilon$ are positive real numbers as revealed from Eq. (5), which can contribute to an increase of Faraday rotation angle $\Theta$. It is known that both dielectric constant and refractive index of TiO$_2$ crystal are larger than those of Al$_2$O$_3$ crystal, 38 although the matrix phase of the present TiO$_2$ and Al$_2$O$_3$ thin films is amorphous as shown in Figs. 1 and 2. Hence, the EuS microcrystal-embedded TiO$_2$ film may manifest larger Faraday rotation angle than the Al$_2$O$_3$ matrix when the amount of EuS is almost the same as each other.

In addition, the large magnitude of the Verdet constant for the TiO$_2$ films is suggestive of the occurrence of quantum confinement effect which leads to the enhancement of Faraday effect in EuS microcrystals. A quantitative analysis of the quantum confinement effect in EuS microcrystals cannot be done at this moment because we have no information about the microstructure of the present films such as the volume fraction and crystallite size of EuS microcrystalline phase. Transmission electron microscopic measurements are required to evaluate the crystallite size of EuS as well as the volume fraction of EuS phase in the TiO$_2$ thin films so that the influence of quantum confinement effect of EuS phase on the Faraday effect can be clarified. In addition, a comparison of the Verdet constant between the present EuS microcrystal-embedded TiO$_2$ films and EuS single crystal or thin film is needed. Such a study is in progress.

V. CONCLUSIONS

EuS microcrystal-embedded Al$_2$O$_3$ and TiO$_2$ thin films were successfully prepared by using rf sputtering method. Faraday effect due to the $4f^7\rightarrow4f^85d$ transition of Eu$^{2+}$ in the EuS microcrystalline phase was clearly observed. In particular, EuS microcrystal-embedded TiO$_2$ thin films exhibit

<table>
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<tbody>
<tr>
<td>Substrate temperature: 200 °C as-deposited</td>
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</tr>
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</tr>
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Fig. 3. Also, the Verdet constants at 500 nm for the SiO$_2$ films, which are about $-0.02$ to $-0.005$ deg/cm Oe (from $-1.2$ to $-0.3$ min/cm Oe), are comparable to those reported for rare-earth-containing glasses. 1-15

A comparison of x-ray diffraction patterns and Mössbauer spectra between Al$_2$O$_3$ and TiO$_2$ thin films reveals that the amount of EuS precipitated is larger in the TiO$_2$ thin films than in the Al$_2$O$_3$ thin films when the preparation condition is the same as each other. This is presumably attributable to the difference in ability to form amorphous state between TiO$_2$ and Al$_2$O$_3$. Kozuka et al. 37 examined the glass-forming region of TiO$_2$–RE$_2$O$_3$ and Al$_2$O$_3$–RE$_2$O$_3$ systems, where RE denotes trivalent rare-earth, by using a twin-roller quenching method. They found that the glass-forming region is somewhat broader for Al$_2$O$_3$–RE$_2$O$_3$ than for TiO$_2$–RE$_2$O$_3$ systems. Hence, it is thought that the amount of Eu$^{2+}$ and Eu$^{3+}$ dissolved into the amorphous matrix is larger in the Al$_2$O$_3$ thin films than in the TiO$_2$ thin films in the present case. In other words, precipitation of EuS can take place more readily in the TiO$_2$ films. Furthermore, the x-ray diffraction peaks are higher and become sharper upon heat treatment for films deposited at room temperature than for films deposited at 200 °C, as shown in Figs. 1 and 2. We speculate that this phenomenon is observed because chemical reactions can take place more readily between EuS and oxides to form amorphous matrix phases at the substrates when the substrate temperature is higher.

The TiO$_2$ film possesses the largest magnitude of the Verdet constant among the present three kinds of host materials. This is partly because the amount of EuS precipitated is the largest in the TiO$_2$ film. Nonetheless, it seems that the difference in magnitude of the Verdet constant between TiO$_2$ and Al$_2$O$_3$ thin films cannot be explained only by the amount of EuS phase. Although the x-ray diffraction patterns in Figs. 1(a) and 2(a) as well as the fraction of Eu$^{2+}$ shown in Table I indicate that the amount of EuS microcrystals in the as-deposited Al$_2$O$_3$ film prepared without heating of substrate [Fig. 2(a)] is almost identical to or slightly larger than the amount of EuS precipitated in the as-deposited TiO$_2$ film prepared at the substrate temperature of 200 °C [Fig. 1(a)], the magnitude of the Verdet constant of the Al$_2$O$_3$ film is smaller than that of the TiO$_2$ film as shown in Table II. One possibility is the effect of the dielectric constant of the host materials. The Faraday rotation angle of several types of composite materials was calculated theoretically by Abe and Gomi. 24 According to their calculation, the Faraday rotation angle of a composite material in which spheres are dispersed in a continuous matrix is affected by both Faraday rotation

TABLE III. Effective transition wavelength $\lambda_t$ in Eq. (2) for EuS-containing SiO$_2$ films.

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large Faraday rotation angle. A comparison of the magnitude of the Verdet constant at a wavelength of 700 nm among the present thin films and rare-earth-containing oxide glasses reveals that the values for the TiO$_2$ thin films are larger by two orders of magnitude than those of rare-earth-containing glasses. Also, the Verdet constant of the TiO$_2$ thin films is comparable to the value for EuSe single crystal. In contrast, when the target material was SiO$_2$, we could not fabricate EuS microcrystal-embedded films. Instead, amorphous films which showed Faraday effect similar to those of rare-earth-containing glasses were obtained.

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