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Research paper

Transient absorption studies on photothermal energy transfer and heat dissipation: Phthalocyanine-based thin films on Bi, Al-substituted DyIG substrates

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ABSTRACT

In this study, we have investigated the photothermal-energy-transfer-based temperature rise in a ferrimagnetic $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film, followed by heat-dissipation-based temperature lowering. A novel method using nanosecond transient absorption spectroscopy is proposed for observing the photothermal energy transfer and heat dissipation. This approach would be useful for developing various types of photofunctional organic-inorganic hybrid materials.

1. Introduction

In a wide range of applications of the photofunctions of organic-inorganic hybrid materials, such as organic light emitting diodes [1] and organic solar cells [2], the heat dissipation from organic materials to inorganic substrates is essential, since the heat generation in the organic active layers, which causes performance degradation, is one of the critical problems [3–6]. In contrast to its importance, the heat transfer from organic materials to inorganic substrates after pulsed laser irradiation has not been investigated in depth, because of the difficulty involved in the direct observation of the heat transfer via the organic-inorganic interface in the range of micrometers and microseconds. On the other hand, recently, we proposed a novel molecule-based magneto-optical memory (Fig. 5 in Ref. [7]) [7–9]. This memory consists of (1) the instant temperature rise due to nanosecond pulsed laser irradiation of the phthalocyanine (Pc)-based thin film, (2) the magnetic circular dichroism spectroscopic monitoring of demagnetization resulting from the temperature rise reaching high Curie temperature (T_c), and (3) the heat transfer from the organic film to the inorganic substrate in a submicrometer-order scale. Here, the key process is the demagnetization of a magnetic substrate using selective pulsed-laser irradiation of an adjacent Pc-based organic thin film (Fig. 1), and therefore, it is crucial to develop a novel method for analyzing the instant heat dissipation between organic and inorganic materials not only for understanding the heat dissipation in photofunctional organic-inorganic hybrid materials but also for developing molecule-based magneto-optical memory.

In this study, we propose a novel approach for observing the photothermal-energy-transfer-based temperature rise and heat-dissipation-based temperature lowering in an inorganic magnetic thin film by applying nanosecond transient absorption spectroscopy to the molecule-based magneto-optical memory: this memory consists of an organic thin film of silicon Pc dimer, $(SiPc)_2$, and a ferrimagnetic Bi, Al-substituted dysprosium iron garnet film, which are deposited step-wise onto a quartz glass substrate. We employed the temperature-dependent electronic absorption spectra of the iron garnet film substrate, and succeeded in demonstrating the usefulness of transient absorption spectroscopy for observing the instant temperature change in the iron garnet film substrate resulting from the heat transfer from the pulsed laser irradiated Pc-based organic thin film. In comparison with the numerically calculated temperature of the magnetic substrate, the observed transient absorption signals are discussed in terms of the temperature change.

2. Experimental

The ferrimagnetic garnet substrate, $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$, was prepared on a quartz glass substrate by the pyrolysis method as previously reported [10,11]. Its thickness was 600 nm, which was measured by cross sectional scanning electron microscopy images. $(SiPc)_2$ was prepared by the previously reported method [12]. The $(SiPc)_2$-based films consisting of $(SiPc)_2$ and poly(vinylidene fluoride) (PVDF) were prepared on the ferrimagnetic garnet thin film by the cast method: A solution of 0.21 mM of $(SiPc)_2$ and 0.6 mg L^{-1}

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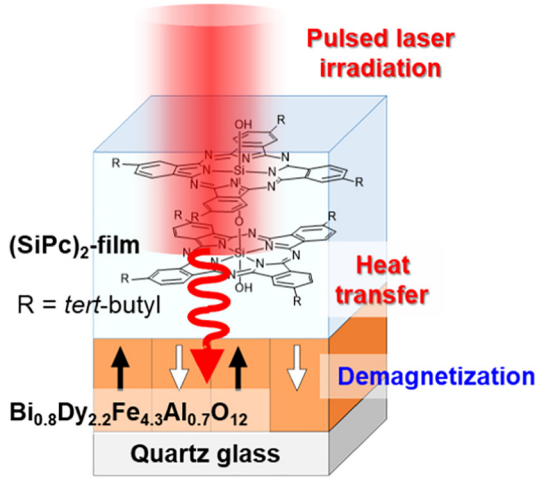

Fig. 1. Pulsed laser irradiation of a molecular thin film of $(SiPc)_2$, followed by the photothermal-energy-transfer-based demagnetization of a ferrimagnetic $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film.

of PVDF in a mixed solvent (toluene:N,N-dimethylformamide = 4:1) was dropped onto an area (5×10 mm^2, determined by masking tape) of each substrate. The thickness of the $(SiPc)_2$-based film was determined to be 200 nm based on the amount of cast compounds.

Diffuse transmission spectra and temperature dependence of absorption spectra were measured using a JASCO U570 spectrophotometer with an integral sphere accessory and a thermostatic circulator accessory, respectively [13]. Transient absorption signals were measured using a monochromator (JASCO CT-25CP) and a photomultiplier (Hamamatsu Photonics R928) with continuous-wave illumination from a Xe lamp (JASCO PS-X150B). In transient absorption measurements, time profiles of the photomultiplier signals were recorded using a digital oscilloscope (Iwatsu-LeCroy LT342). Samples were excited at 640 nm using a dye laser (Sirah CSTR-LG532-TRI-T) pumped with an Nd:YAG laser (Spectra Physics INDI 40; 532 nm; 7 ns pulse width (FWHM)): The incident laser energy was adjusted to 8.4 mJ/pulse.

3. Results and discussion

3.1. Electronic absorption spectra

Fig. 2 shows electronic absorption spectra of the $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film and the $(SiPc)_2$-based film on the $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film at room temperature (20 °C). In the diffuse transmission spectrum of the $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film without the $(SiPc)_2$-based film, a broad band due to the magnetic substrate is observed at around 450 nm [8,9]. In the case of the $(SiPc)_2$-based film on the $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film, in addition to an absorption band of the magnetic substrate at 400–500 nm, a sharp Q absorption band of $(SiPc)_2$ is seen at around 640 nm, which is similar to that of $(SiPc)_2$ in conventional organic solvents [7]. Fig. 2b shows temperature dependence of electronic absorption spectra of the $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film. Further, their temperature difference spectra are shown in Fig. 2c. Upon increasing the temperature from 20 °C to 90 °C, although the absorbance at 450 nm decreased, that at 520 nm increased. This indicates the broadening of the shoulder at 450 nm with increasing temperature, which is consistent with the previous study on the absorption spectra of garnet analogue at low temperature [14]. Thus, the temperature rise should be monitored by the transient absorption at 520 nm and bleaching at 450 nm after pulsed laser irradiation.

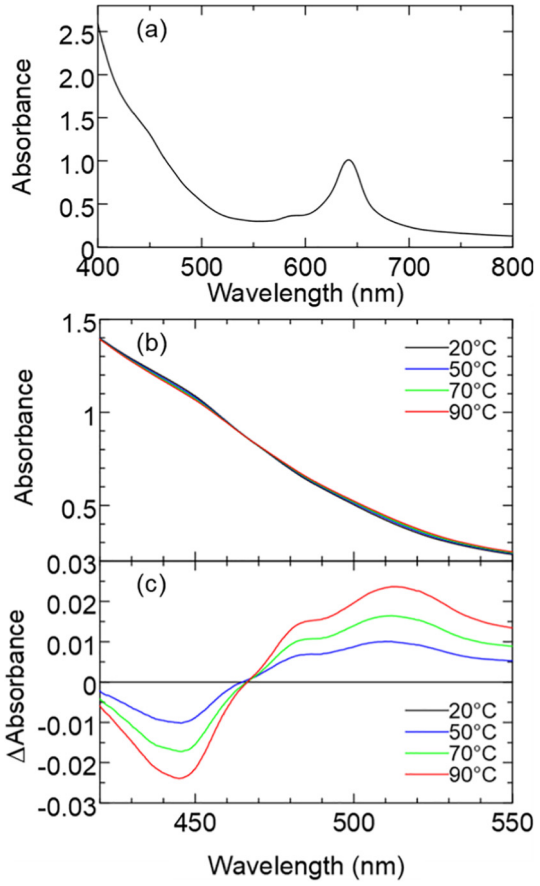

Fig. 2. Diffuse transmission spectra of the $(SiPc)_2$-based film on $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ (a), temperature dependence of electronic absorption spectra of the $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film (b), and temperature difference spectra of the $Bi_{0.8}Dy_{2.2}Fe_{4.3}Al_{0.7}O_{12}$ thin film (c). The difference spectra were obtained by subtracting the spectrum at 20 °C from the spectra at the corresponding temperature.

3.2. Time profiles of transient absorption signals

Fig. 3a and b show the time profiles of transient absorption signals at 450 nm and 520 nm, respectively, after the selective pulsed laser excitation (640 nm) of the $(SiPc)_2$-based film. At 520 nm, the

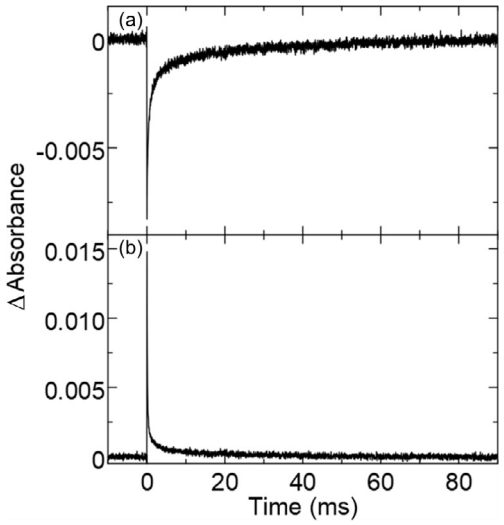

Fig. 3. Time profiles of transient absorption signals at 450 nm (a) and 520 nm (b).