Optical Memory Effect by Interference of Multiple-Scattered Light in a Fluorescent Fulgide Derivative

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Abstract We report an observation of a new wavelength- and angle-selective optical memory effect caused by interference of multiple-scattered light in polystyrene powder doped with a fluorescent fulgide derivative. This effect is applicable to three-dimensional optical data storage.

Keywords fulgide; polystyrene; interference; multiple scattering; optical memory; three-dimensional data storage

INTRODUCTION

Recently we have revealed that photoreactive materials combined with strongly scattering host media cause a novel optical memory effect, which is potentially applicable to high density optical data storage. We have discovered it in Sm-doped ZnS nanocrystals[1, 2]. The effect was observed in the excitation spectrum of the fluorescence of Sm ions; a hole was found to persist in the spectrum after irradiation of monochromatic light. If one looks at this result alone, one might consider the effect to be nothing but the persistent spectral hole-burning[3]. However, the hole was observed when not only the wavelength but also the incident angle of the probe light coincided with those of the recording light. This observation indicates that this effect differs from the conventional persistent hole burning in kind.

We have shown the mechanism of this effect to be as follows[1]. In the

recording process, an interference pattern of multiple-scattered light within the medium, which is dependent on both the wavelength and the incident angle of the recording light, is registered by photobleaching of Sm as a spatial modulation of the absorbance. In the reading process, intensity of the fluorescence from the sample is measured. The intensity is proportional to the overlap integral between the spatially modulated absorbance created by the recording light and the interference pattern formed by the reading, or exciting, light. Thus, the fluorescence intensity shows a dip when both the wavelength and the incident angle of the reading light coincide with those of the recording light, because, in this situation, the absorbance and the intensity of the reading light at each position in the sample alternate with each other, and the excitation is less effective.

Necessary conditions for this effect are that (1) the recording medium is photoreactive, (2) the medium is fluorescent, and the fluorescence intensity is changed according to the photoreaction, and (3) the medium is optically inhomogeneous and causes multiple-scattering of light in it. Then we inferred that this effect is quite common and can be observed in other combinations of multiple-scattering media and photoreactive materials. Binaphthol-condensed indolylfulgide is a suitable photoreactive material for a possible observation of this effect because it shows photochromism and its colored form is fluorescent[4]. We designed a recording medium by combining the fulgide with a scattering host consisting of polystyrene to prove generality of this effect. In this paper, we report the fundamental properties of this recording medium and the wavelength- and angle-multiplexed optical memory effect observed in it.

EXPERIMENTAL

Synthesis of binaphthol-condensed indolylfulgide has been already reported[5]. This fulgide derivative is one of a few fluorescent photochromic molecules. Both of the colored C-form and the colorless E-form are thermally stable, and the C-form is transformed to the E-form by the irradiation within the absorption band in the visible region. When each form in toluene is excited within respective absorption bands at room temperature, the C-form (absorption maximum 471 nm) emits fluorescence (fluorescence maximum 640 nm), while the E-form (absorption maximum 368 nm) does not[4]. In order to observe the optical memory effect by the recording of the interference pattern, fulgide must be doped into a solid host which strongly scatters light within it. Thus we prepared a polystyrene film doped with the fulgide derivative (1.2 wt %) and ground it into fine powder. Obser-

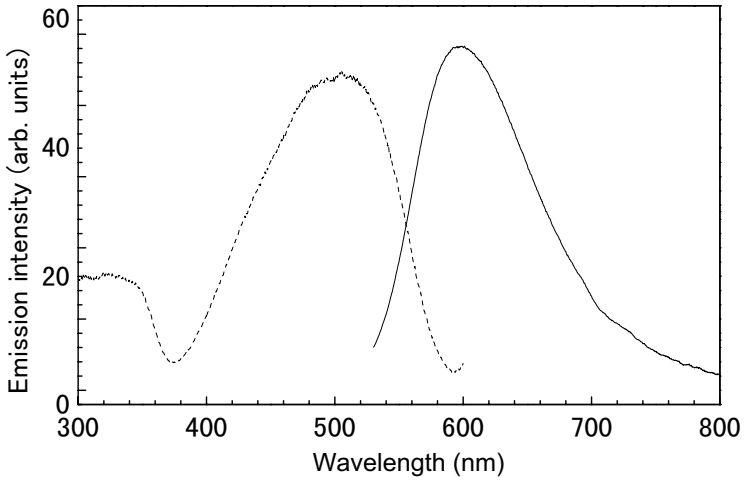

FIGURE 1 Excitation spectrum of the emission at 630 nm (dashed line), and emission spectrum excited at 500 nm (solid line) of the C-form of binaphthol-condensed indolylfulgide in polystyrene powder.

vation by a scanning electron microscope showed that the powder sample was composed of grains of the order of 1 μm. The polystyrene powder is expected to act as an effective scatterer for visible light because of this structural inhomogeneity.

Excitation and emission spectra were measured by using a spectrophotometer (Hitachi F4500). In the measurement of the memory effect, the sample was placed on a stage equipped with a computer-controlled micrometer, which rotates the stage around an axis lying in its surface to scan the angle of the incident beam relative to the surface normal. The minimum step of the rotating angle was 0.0028°. The sample was irradiated by attenuated light from a cw dye laser or an Ar-ion laser, and the wavelength or the incident angle of the laser light was scanned while the fluorescence with the wavelengths longer than 590 nm was detected through cutoff filters by a photomultiplier; the same laser beam was used for burning the holes, but the intensity was about 10^4 times higher than that for the fluorescence measurements. All the experiments were made at room temperature

RESULTS AND DISCUSSION

Since the sample is powder, we measured the excitation spectrum instead of the absorption spectrum. Figure 1 shows the excitation and the emission

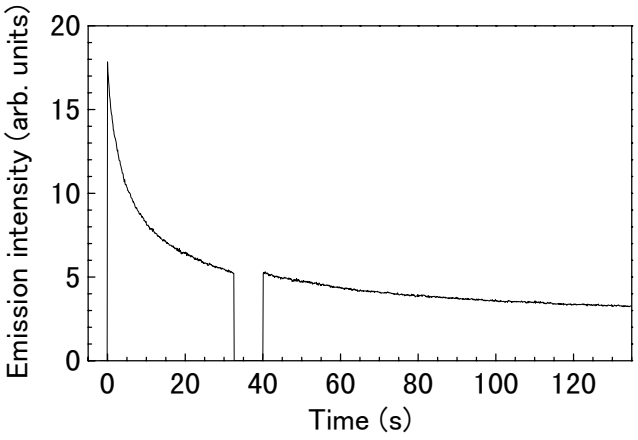

FIGURE 2 Decay of the fluorescence intensity of the C-form fulgide in polystyrene powder caused by the light irradiation (wavelength 514.5 nm, intensity 0.5 mW/mm^2).

spectra of the C-form fulgide in polystyrene powder. In polystyrene, Stokes shift is smaller than in toluene, and the excitation and the fluorescence maxima are 505 nm and 597 nm, respectively.

Figure 2 shows the decay of the fluorescence intensity around 600 nm by the irradiation of 514.5 nm light. Irradiation was suspended momentarily from 33 to 40 s in order to check the stability of the product state. The fluorescence intensity showed a smooth decay curve if the suspension period was cut out, which indicates that the back reaction in the dark is negligible. The decay curve is non-exponential as has been often observed in photochromic materials in solid matrices[6]. The curve in Figure 2 can be fitted by an empirical function $a+b/\sqrt{1+ct}$ very well, where t is the irradiation time, a, b and c are adjustable parameters. The fluorescence intensity does not decay toward zero, which means that the C-form in polystyrene is not completely converted to the E-form.

We measured the angular dependence of the backscattered light from the sample by using 633 nm light of a He-Ne laser. In multiple-scattering media, a constructive interference of time-reversed counter-propagating waves is known to enhance the intensity of the scattered light in the exact backward direction[7]. The peak observed in the scattered light around the backward direction is called coherent backscattering cone. In the present polystyrene powder sample, a coherent backscattering cone similar to that of Sm-doped ZnS nanocrystals[2] was observed. This result indicates that

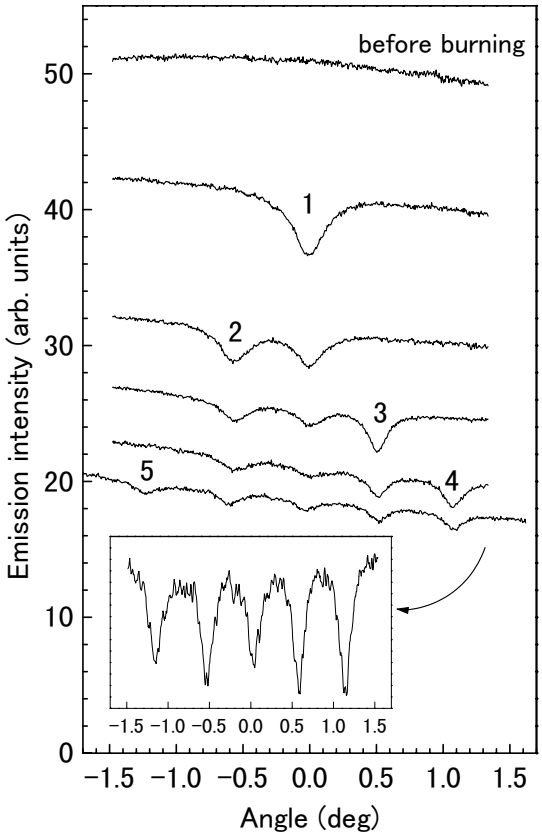

FIGURE 3 Profile of successively burned five holes. Emission intensity was measured as a function of the incident angle. After the measurement of the initial profile before the burning, holes were burned at different incident angles indicated by the numerals(wavelength 488 nm, intensity 0.5 mW/mm^2, burning time 20 s for each hole) and then the profiles were measured. The final profile with five holes is enlarged in the inset.

the polystyrene powder has the scattering strength comparable to ZnS nanocrystals. The FWHM of the backscattering cone was 0.41°, from which the mean free path of light in the sample is estimated at 15 μm according to ref. [7].

Now that it was confirmed that the polystyrene powder doped with the fulgide derivative fulfills the necessary conditions, we tried to observe the optical memory effect caused by interference of multiple-scattered light. Figure 3 shows the result of an experiment to burn multiple holes at differ-

ent incident angles. The holes are clearly observed after each irradiation, and the fact that they are dependent on the incident angle signifies that the observed holes are due to interference. Besides the holes, there exists almost uniform decrease of the emission intensity after every irradiation, which has been observed also in Sm-doped ZnS nanocrystals[1]. This uniform decrease is an indication that this effect stems from a nonlocal interference effect, in which a writing action at any writing angle more or less affects the fluorescence intensity at all the reading angles. With the sequence of the hole burning, previously burned holes are getting shallower but they show no broadening at all. Therefore, in principle, a large number of holes can be recorded in a single recording area.

The hole width shown in Figure 3 is about 0.33°, while the width of the hole measured as a function of the wave number was about 5 cm^{-1}. If the hole can be burned all over the solid angle 2π of the incident light, the angular multiplicity is about 1.9×10^5. The wavelength multiplicity is estimated at about 1500 from the width of the excitation band shown in Figure 1. The size of the recording area is considered to correspond to the distance between the impinging points of the interfering waves on the sample[2], which is estimated from the angular width of the hole to be 85 μm. Accordingly, the surface density of the memory amounts to 39000 bit/μm^2. This extremely high storage density comes from the fact that information is stored in the body of the medium as a three-dimensional interference pattern. This method has an advantage over other three-dimensional optical data storage methods, because information is stored and retrieved by a simple way of changing the wavelength and the incident angle of light.

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