Photobrightening of photodarkened CdS- and CdS_xSe_{1-x}-doped glasses

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Photobrightening of photodarkened CdS- and CdS_xSe_{1-x}-doped glasses was investigated using luminescence and electron spin resonance (ESR). Photobrightening depends on wavelength of laser light, and it is observed in all samples investigated, when wavelength of laser light is longer than that of absorption edge. Photobrightening depends on glass composition.

1. Introduction

Since Jain and Lind [1] first reported that semiconductor-doped glasses have a large optical nonlinearity and a fast response time, the optical properties of these materials have been investigated extensively. Roussignol *et al*. [2] reported that the response time of the nonlinear signal and the luminescence of CdS_xSe_{1-x}-doped glass shortened upon light irradiation. This photoinduced irreversible process is called photodarkening. Photodarkening is considered to be due to defect centers, which are activated upon light irradiation and act as nonradiative recombination centers [3–5]. Therefore, the decay time and the intensity of the luminescence decrease. When photodarkened glass is heated to 400–450°C for a few hours, it recovers its original properties [2]. In a previous paper [6], we reported that the intensity and decay time of luminescence from photodarkened CdS-doped glass, Toshiba Y-44, increased upon light irradiation with wavelength of about 500 nm. This result indicates that reverse process of photodarkening (photobrightening) occurrs in CdS-doped glass upon light irradiation. On the other hand, it is reported that photodarkening depends on manufacturers of glasses [7–9]. While Toshiba sample shows strong photodarkening, Corning sample shows weak photodarkening. Here, we report the effect of light irradiation on photodarkened CdS-doped glasses from different manufacturers to investigate the possibility of photobrightening in Corning and other samples. We also report the effect of wavelength of absorption edge on photobrightening in CdS_xSe_{1-x}-doped glasses.

2. Experimental procedure

The samples investigated were commercial CdS-doped filter glasses whose absorption edge is near 440 nm from different manufacturers: Toshiba Y-44, Hoya Y-44, Schott GG435 and Corning 3-73. We also investigated other CdS-doped filter glasses, Toshiba Y-45, Y-46 and Y-48, and CdS_xSe_{1-x}-doped filter glasses, Toshiba Y-50, Y-52, O-54 and O-56. Absorption edges of these glasses are about 450 nm (Y-45)–560 nm (O-56). The size of samples was $2.5 \times 2.5 \times 25$ mm^3. The concentration of CdS or CdS_xSe_{1-x} was about 0.4 wt%. The glass was exposed to pulsed light from a frequency-tripled Nd:YAG laser (Quanta-Ray GCR-230T-10; wavelength = 355 nm, pulse duration = 5 ns, repetition rate = 11 Hz, peak power density = 5 MW/cm^2) for 2 min, and then exposed to pulsed light from an optical parametric oscillator (Quanta-Ray MOPO-700; pulse duration = 5 ns, repetition rate = 11 Hz, peak power density = 10 MW/cm^2) for 8 min (Y-44, GG435 and 3-73) or 4 min (other glasses) at 300 K.

Transient characteristics of luminescence were measured using the following apparatus at 300 K. The excitation source was a frequency-doubled Ti:sapphire laser with a pulse selector (Spectra Physics Tsunami 3960 and 3980; wavelength = 390 nm, pulse duration = 200 fs, peak power density = 0.5 MW/cm^2, repetition rate = 4 MHz). The decay time of the luminescene was measured at 300 K using a streak camera (Hamamatsu C4334). The ESR spectra were measured at 77 K using an X-band spectrometer (JES FE-1X). The *g*-values of the signals were determined using a MgO : Mn marker.

3. Results and discussion

When we used the Ti:sapphire laser as the excitation source, we observed luminescence band at about 440 nm for CdS-doped glasses. This band is attributable to the band-to-band type or shallow-trapping state-to-band-type transition [10]. Transient characteristics of luminescence change after irradiation. Although luminescence intensity decays nonexponentially [11], initial decay of luminescence intensity is approximately

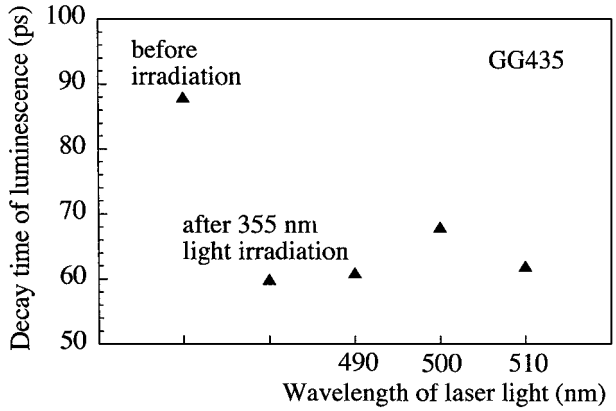

Figure 1 Decay time of luminescence from CdS-doped glass, Schott GG435, at peak wavelength (440 nm) as a function of wavelength of laser light for the second irradiation.

regarded as exponential. Thus, we use t_d as the measure of decay time,

$$t_d = -\{10 \ln[I(0.1)/I(0)]\}^{-1}, \qquad (1)$$

where $I(0)$ is luminescence intensity at $t = 0$ ns (zero time delay) and $I(0.1)$ is that at $t = 0.1$ ns. Fig. 1 shows decay time of luminescence from CdS-doped glass, Schott GG435, at peak wavelength. We used five samples to obtain the data points. Sample 1 was not exposed to laser light. Sample 2 was exposed to laser light with wavelength of 355 nm. Samples 3, 4 and 5 were exposed to laser light with wavelength of 355 nm, and then exposed to laser light with wavelength of 490 nm, 500 nm and 510 nm, respectively. The decay time decreases upon 355 nm light irradiation, and then increases upon the second irradiation with wavelength of about 500 nm. When the wavelength of light from the optical parametric oscillator is tuned at 500 nm, the longest decay time is observed. We also observed increase in the luminescence intensity upon 500 nm light irradiation. These results are similar to those in Toshiba Y-44 [6].

Photodarkening and photobrightening are explained by the following processes (Fig. 3 in ref. [6]). Electrons in the valence band of CdS nanocrystals are excited to the conduction band, some of which relax to traps at the glass-semiconductor interface. Before the electrons recombine, laser light reexcites some of these trapped electrons to higher-energy surface states, from which they migrate into the glass. These electrons eventually relax to deep levels in glass. The two-step excitation process of electrons via trap levels was proposed by Malhotra *et al.* [12], and confirmed by us [13]. Photogenerated holes in CdS nanocrystals migrate into the interface region between CdS nanocrystals and the glass matrix, and they activate defect centers. The activated defect centers act as nonradiative recombination centers, and they cause decrease in the intensity and the decay time of luminescence (photodarkening). Photodarkening is not observed in trap free glasses [14]. This result is consistent with the two-step excitation process. In addition to these processes, laser light reexcites some of the trapped electrons to the conduction band of glass, and some electrons recombine with holes and passivate the defect centers [6]. The passivation of the activated defect centers causes increase in the intensity and the decay time of luminescence (photobrightening). Light with wavelength longer than 500 nm cannot generate carriers in CdS nanocrystals in Y-44 and does not activate the defect centers. However, this light may excite the trapped electrons in glass to the conduction band of glass, to passivate the defect centers. Thus the decay time of luminescence associated with the activated defect centers increases upon laser irradiation at a wavelength of 500 nm. The most efficient wavelength for photobrightening is 500 nm in Y-44.

The increase in the decay time and the luminescence intensity is also observed in the other photodarkened samples, Hoya Y-44 and Corning 3-73, after the second irradiation of 500 nm light. Fig. 2 shows the relative values of decay times of luminescence, $t_d(355–500)/t_d(355)$, where $t_d(355–500)$ is the decay time of luminescence of the CdS-doped glass after 355 nm and 500 nm light irradiation, $t_d(355)$ is that after 355 nm light irradiation. The change in the decay time is largest for Toshiba Y-44 and smallest for Corning 3-73.

We measured ESR spectra to investigate the effects of light irradiation on defect centers in glasses. Fig. 3 shows ESR spectrum of CdS-doped glass, Schott GG435, at 77 K before and after light irradiation. The signal near $g = 2.01$ is caused by activated defect centers (trapped holes on the defect centers) at the interface region between CdS nanocrystals and the glass matrix

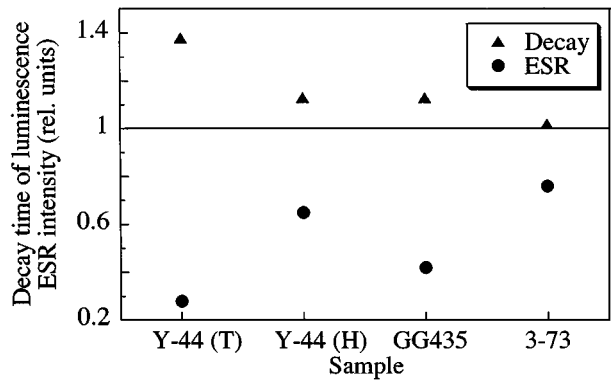

Figure 2 Relative values of decay times of luminescence and intensities of the ESR signals of the photodarkened CdS-doped glasses.

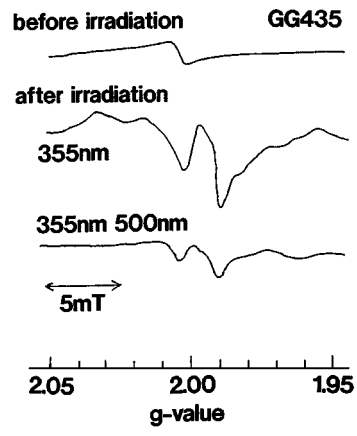

Figure 3 ESR spectrum of CdS-doped glass, Schott GG435, at 77 K.

and associated with photodarkening [4]. The signal near $g = 1.99$ is considered to be due to trapped electrons on Cd^{2+} ions in the glass [15]. The intensity of these signals increases after 355 nm light irradiation. When the photodarkened glasses are exposed to light with wavelength of about 500 nm, the intensities of the ESR signals decrease. The decrease in the intensity of the signal near $g = 1.99$ indicates that electrons trapped in the glass are detrapped. The decrease in the intensity of the signal near $g = 2.01$ indicates that holes on the defect centers recombine with the detrapped electrons. Fig. 2 shows the relative values of the ESR signals, $I(355–500)/I(355)$, where $I(355–500)$ is the intensity of the ESR signal near $g = 2.01$ of the CdS-doped glass after 355 nm and 500 nm light irradiation, and $I(355)$ is that after 355 nm light irradiation. The change in the signal near $g = 2.01$ is almost correlated with change in the decay time of luminescence. The results indicate that the defect centers are activated upon light irradiation with wavelength of 355 nm and partly passivated upon the second irradiation with wavelength of about 500 nm for all samples investigated. The largest change is observed for Toshiba Y-44, and the smallest one for Corning 3-73. This result indicates that photobrightening easily occurrs in Toshiba Y-44, and hardly occurrs in Corning 3-73. We have already observed that photodarkening easily occurrs in Toshiba Y-44, and hardly occurrs in Corning 3-73 [9]. Thus, activation and passivation easily occur in Toshiba Y-44 and hardly occur in Corning 3-73. Both processes depend on glass composition. Since laser light with wavelength of about 500 nm is only slightly absorbed by glass and the beam size is large (6 mm in diameter), the laser heating effect is negligibly small. Thus, passivation of the defect centers is caused by photons instead of by laser heating.

We also investigated laser-induced brightening in other CdS- and CdS_xSe_{1-x}-doped glasses of Toshiba, since photobrightening is most effective in glass of Toshiba, Fig. 4 shows decay time of luminescence from photodarkened CdS_xSe_{1-x}-doped glass, Toshiba O-54, at peak wavelength. The decay time decreases upon 355 nm light irradiation, and then increases upon the second irradiation. When the wavelength of light from the optical parametric oscillator is tuned at 590 nm, the longest decay time is observed. The most efficient wavelength for laser-induced brightening depends on absorption edge of semiconductor nanocrystals. Light with wavelength longer than 500 nm cannot generate carriers in CdS nanocrystals in Y-44 and does not activate the defect centers. Thus the most efficient wavelength for photobrightening is 500 nm in Y-44. On the other hand, light with wavelength longer than 500 nm can generate carriers in CdS_xSe_{1-x} nanocrystals in O-54 and activate the defect centers, since absorption edge of O-54 is 100 nm longer than that of Y-44. Light with wavelength longer than 590 nm cannot generate carriers in CdS_xSe_{1-x} nanocrystals in O-54 and does not activate the defect centers. This light may excite the trapped electrons in glass to the conduction band of glass, to passivate the defect centers. Thus, the most efficient wavelength for photobrightening is 590 nm in O-54. The most efficient wavelength for photobrightening shifts to longer wavelength, when absorption edge becomes longer: 510 nm (Y-45), 530 nm (Y-46), 540 nm (Y-48), 560 nm (Y-50), 570 nm (Y-52), 590 nm (O-54) and 620 nm (O-56).

We also investigated photobrightening as a function of irradiation time. Fig. 5 shows luminescence intensity of photodarkened CdS-doped glass, Toshiba Y-45, as a function of irradiation time of 532 nm light. We

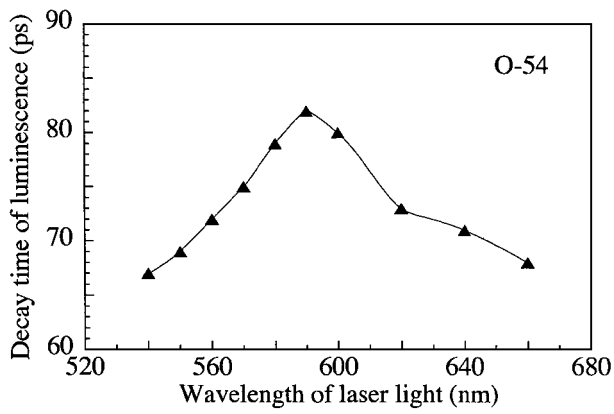

Figure 4 Decay time of luminescence from photodarkened CdS_xSe_{1-x}-doped glass, Toshiba O-54, at peak wavelength (540 nm) as a function of wavelength of laser light for the second irradiation. Decay times are about 200 ps for unirradiated sample and 60 ps for sample after 355 nm light irradiation. A curve was drawn through the data points as a guide for the eyes.

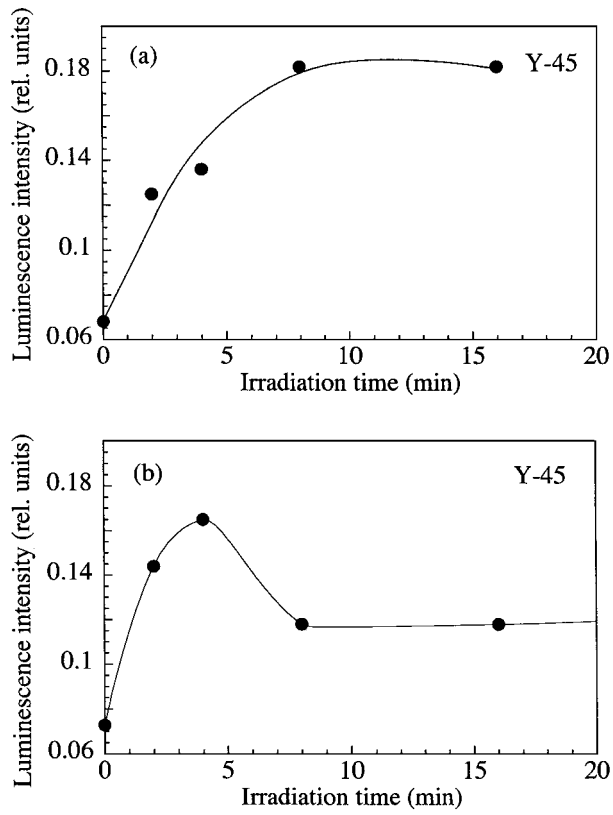

Figure 5 Luminescence intensity of photodarkened CdS-doped glass, Toshiba Y-45 as a function of irradiation time of laser light for the second irradiation. The peak power density of 355 nm light is 1.3 MW/cm^2, and the peak power density of 532 nm light is 2.5 MW/cm^2 (a) and 5 MW/cm^2 (b). Luminescence intensity is the relative value to that of the unirradiated sample. Curves were drawn through the data points as a guide for the eyes.

used pulsed light from the frequency-doubled Nd:YAG laser instead of the optical parametric oscillator, since light intensity for the former is more stable than that for the latter. When the laser power of 532 nm light is 2.5 MW/cm^2 (Fig. 5a), the luminescence intensity increases with irradiation time, and then saturates. Since number of trapped electrons in glass is finite, photobrightening should show saturation as a function of irradiation time. When the laser power is 5 MW/cm^2 (Fig. 5b), the luminescence intensity increases with irradiation time, reaches maximum, and then decreases. If 532 nm light causes photodarkening, this decrease in the luminescence intensity is due to photodarkening. We measured luminescence intensity of Y-45 after irradiation of 532 nm light only. However, we observed no change in the luminescence intensity. Thus, we must use more complicated model than that shown in Fig. 3 in ref. [6] to explain the decrease in the luminescence intensity for longer irradiation time.

4. Summary

The luminescence and ESR spectra were measured in CdS- and CdS_xSe_{1-x}-doped glasses. When photodarkened CdS-doped glasses, Y-44, GG435 and 3-73, are exposed to 500 nm light, the intensity and the decay time of luminescence increase. Photobrightening depends on glass composition and wavelength of laser light, and it occurrs, when wavelength of laser light is longer than that of absorption edge.

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References

1. R. K. JAIN and R. C. LIND, *J. Opt. Soc. Am.* **73** (1983) 647.
2. P. ROUSSIGNOL, D. RICARD, J. LUKASIK and C. FLYTZANIS, *J. Opt. Soc. Am. B* **4** (1987) 5.
3. T. MIYOSHI, K. TOWATA and N. MATSUO, in Proc. Int. Conf. Optical Properties of Nanostructures, Sendai, 1994; *Jpn. J. Appl. Phys.* **34**(Suppl. 34-1) (1995) 46.
4. *Idem., Jpn. J. Appl. Phys.* **33** (1994) 6299.
5. T. MIYOSHI, K. TOWATA, H. MATSUKI, N. MATSUO and T. KANEDA, *Materials Sci. Forum* **196–201** (1995) 573.
6. T. MIYOSHI, K. NITTA, H. OHKUNI, F. IKEDA and N. MATSUO, *Jpn. J. Appl. Phys.* **36** (1997) 6726.
7. N. HORIUCHI and Y. UESU, *Waseda Daigaku Rikogaku Kenkyusho Hokokushu* **137** (1992) 43. [in Japanese].
8. T. YANAGAWA, H. NAKANO, Y. ISHIDA and K. KUBODERA, *Optics Commun.* **100** (1993) 118.
9. T. KANADA, T. MIYOSHI, S. NISHIMURA and N. MATSUO, *J. Mater. Sci.* **34** (1999) 1519.
10. K. MISAWA, H. YAO, T. HAYASHI and T. KOBAYASHI, *Chem. Phys. Lett.* **183** (1991) 113.
11. M. TOMITA and M. MATSUOKA, *J. Opt. Soc. Am. B* **7** (1990) 1198.
12. J. MALHOTRA, D. J. HAGAN and B. G. POTTER, *ibid.* **8** (1991) 1531.
13. T. MIYOSHI, K. NITTA, H. OHKUNI, K. SHIRAISHI and N. MATSUO, *Jpn. J. Appl. Phys.* **37** (1998) 4330.
14. Y. ASAHARA, *Ceramics Int.* **23** (1997) 375.
15. T. MIYOSHI, H. FURUKAWA, K. NITTA, H. OKUNI and N. MATSUO, *Solid State Commun.* **104** (1997) 451.

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