Photodarkening and photobrightening in CdS-doped glasses

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Abstract Photobrightening of photodarkened CdS-doped glasses has been investigated using luminescence experiments after irradiation of laser light with the wavelength longer than that of the absorption edge. The photoluminescence intensity increases with irradiation time, reaches a maximum, and then decreases. This result is explained by considering the reexcitation of trapped electrons in glass. The location of the traps is investigated using thermoluminescence experiment.

1 Introduction

Semiconductor-doped glasses have large optical nonlinearity with a fast response time. The decay time and intensity of luminescence from CdSSe-doped glasses decrease upon light irradiation [1]. This photoinduced irreversible process is called photodarkening. On the other hand, we observed 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 [2]. This result indicates that the reverse process of photodarkening (photobrightening) occurrs in CdS-doped glass upon light irradiation.

Photodarkening and photobrightening are explained by the following processes. Electrons in the valence band of CdS nanocrystals are excited to the conduction band upon 355 nm light irradiation, they migrate into the glass, and they are trapped in the glass matrix [3]. On the other hand, photogenerated holes in CdS nanocrystals migrate into the interface region between CdS nanocrystals and the glass matrix, and they are trapped at defect centers. The centers act as nonradiative recombination centers, since photogenerated electrons in semiconductor nanocrystals may recombine nonradiatively with holes trapped at the defect centers. Thus, they cause a decrease in the luminescence intensity (photodarkening). On the contrary, 500 nm light cannot generate carriers in CdS nanocrystals. However, this light may excite trapped electrons in the glass to the conduction band of the glass, they migrate into CdS-nanocrystals, and some electrons recombine with holes at the defect centers and passivate the defect centers. The passivation of the defect centers causes an increase in the luminescence intensity (photobrightening) [2]. Here, we report photobrightening as a function of irradiation time in Y-44 and other samples. We also measured thermoluminescence (TL) of photodarkened CdS-doped glasses to investigate the traps in glasses.

2 Experimental procedure

The samples investigated were commercial CdS-doped filter glasses, Toshiba Y-44, Y-45, Y-46, Y-47 and Y-48, since filter glasses of Toshiba showed the most noticeable photobrightening among the following manufacturers: Toshiba, Hoya, Schott and Corning. Absorption edges of these glasses are about 440 nm for Y-44 and 480 nm for Y-48. The concentration of CdS was 0.4 wt%. The glasses were 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 = 1.3 MW/cm^2) for 2 min (first irradiation), and then exposed to pulsed light from the frequency-doubled Nd:YAG laser (Quanta-Ray GCR-230T-10; wavelength = 532 nm, pulse duration = 5 ns, repetition rate = 11 Hz, peak power density = 5 MW/cm^2) at 300 K (second irradiation).

The luminescence intensity was measured at 300 K using an N_2 laser (Laser Photonics LN120; wavelength = 337.1 nm, pulse duration = 0.3 ns, repetition rate = 4 Hz, peak power density = 50 kW/cm^2) and a photomultiplier (Hamamatsu R456). TL was measured using a TLD reader (Kyokko 2500). TL measurements were performed by heating the photodarkened sample up to 500° C. The heating rate was 470° C/min. The glow curve was recorded using a pen recorder.

3 Results and discussion

Photobrightening was observed in all samples investigated. We investigated photobrightening as a function of irradiation time of the second irradiation. Figure 1 shows the luminescence intensity of photodarkened CdS-doped glasses, Y-44, Y-46 and Y-48, as a function of irradiation time with 532 nm light. The luminescence intensity of Y-44 increases with irradiation time, and tends to saturate. On the other hand, the luminescence intensities of other samples increase with irradiation time, reach maxima, and then decrease. This decrease in the luminescence intensity is considered to be due to photodarkening. A small number of electrons may be generated in semiconductor nanocrystals by the irradiation with 532 nm light. Photogenerated electrons are trapped in glass. Although the traps in glass are distributed energetically, we classify them: T_1 represents shallower traps and T_2 represents deeper traps. Since the energy level of T_1 is shallower, the trapped electrons in T_1 are excited to the conduction band of glass upon irradiation with 532 nm light. The number of trapped electrons, N_1, decreases with irradiation time, and then becomes constant. On the other hand, the energy level of T_2 is deeper. Thus, the trapped electrons are not excited to the conduction band of glass upon irradiation with the 532 nm light. The number of trapped electrons, N_2, increases with irradiation time, since electrons are supplied from semiconductor nanocrystals. The total number of N_1 and N_2 decreases with irradiation time, reaches a minimum, and then increases. Since the luminescence intensity is approximately proportional to the inverse of $(N_1 + N_2)$, it should increase with irradiation time, reach a maximum, and then decrease.

We consider rate equations for electrons [4]. The rate equations for trapped electrons, N_1 and N_2, are

$$dN_1/dt = AJ^2 - BN_1J, \quad (1)$$

$$dN_2/dt = AJ^2, \quad (2)$$

where J is the irradiation intensity and A and B are rate constants. The first terms on the right-hand side in eqs. (1) and (2) express the trapping process of electrons. Since the trapping occurs via a two-step excitation process [5], these terms are proportional to J^2. The second term on the right-hand side in eq. (1) expresses the reexcitation of the trapped electrons. The inset in Fig. 1 shows the calculated results of $1/(N_1 + N_2)$ for Y-44, Y-46 and Y-48. We consider that semiconductor nanocrystals in Y-44 do not absorb 532 nm light, since band gap of semiconductor nanocrystals in Y-44 is larger than that of other samples. Thus, the value of A in eqs. (1) and (2) becomes 0 for Y-44. Since band gap of semiconductor nanocrystals in Y-48 is smaller than that of Y-46, the value of A for Y-48 is larger than that for Y-46. The calculated results reproduce the experimental results. The decay time of luminescence as a function of irradiation time shows similar behavior to that of the intensity of luminescence shown in Fig. 1 [4].

Since trapped electrons in glass are considered to be excited by 532 nm light and recombine with holes in semiconductor nanocrystals, photostimulated luminescence (PSL) is expected to be observed in photodarkened CdS-doped glasses under 532 nm light excitation. However, this is experimentally difficult to perform, since intense 532 nm light interferes with the observation of PSL. Thus, we observed TL instead of PSL. Figure 2 shows glow curve of TL of Y-44. Other samples show similar glow curves to that of Y-44. From the glow curve, we estimated the location of traps to be about 1 eV below the conduction band of glass. Since the traps are thought to be distributed in energy, this value shows the upper bound of the distribution. TL is not observed in CdS-doped glasses before 355 nm light irradiation.

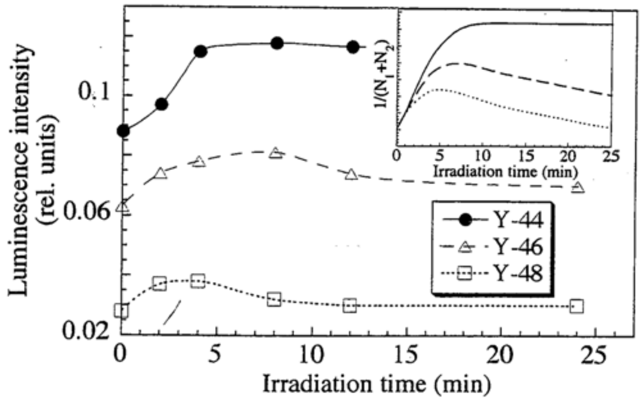

Fig. 1 Luminescence intensity of photodarkened CdS-doped glasses, Toshiba Y-44, Y-46 and Y-48, as a function of irradiation time with 532 nm light. Inset: Calculated results of $1/(N_1 + N_2)$ as a function of irradiation time. $(N_1 + N_2)$ is the number of trapped electrons in glass. The parameters used for this calculation are as follows: $J = 20$, $N_{10} = 100$, $N_{20} = 30$, $A = 0$ (Y-44), 0.003 (Y-46), 0.008 (Y-48) and $B = 0.03$, where N_{10} is the value of N_1 at $t = 0$ and N_{20} is the value of N_2 at $t = 0$. There is meaning in the relative values of the parameters.

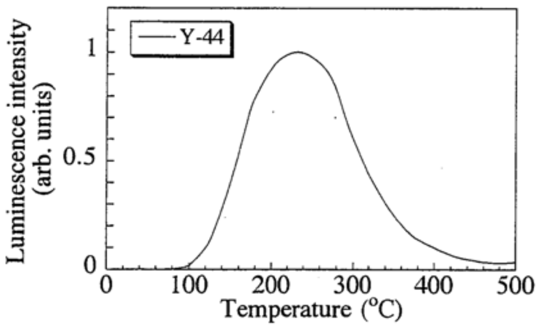

Fig. 2 Glow curve of thermoluminescence of photodarkened CdS-doped glass, Y-44.

4 Summary

Luminescence was measured in the photodarkened CdS-doped glasses after irradiation of laser light with wavelength longer than that of the absorption edge. The luminescence intensity increases with irradiation time, reaches a maximum, and then decreases. This result is explained by a model, which considers the reexcitation of trapped electrons in glass.

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