PHOTOINDUCED DEFECTS IN CdS-DOPED GLASSES

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Keywords: photodarkening, semiconductor, microcrystal, quantum dot, luminescence, ESR

Abstract. Photoinduced defects in CdS-doped glasses were investigated using luminescence and electron spin resonance (ESR). Correlation between the intensity of ESR signal and the transient characteristics of luminescence was observed. This correlation suggests that the photoinduced centers responsible for the ESR signal cause photodarkening. The photoinduced centers are considered to be created in the interface region between CdS microcrystals and glass matrix.

Introduction

Semiconductor-doped glasses have been investigated extensively as materials for optoelectronics. In these glasses, semiconductor microcrystals with diameter of about 10 nm are embedded in bulk-glasses. Semiconductor-doped glasses have large optical nonlinearity with a fast response time[1]. Roussignol et al.[2] reported that the response time of nonlinear signal and luminescence of CdSSe-doped glass decreased by light irradiation. This photoinduced irreversible process is called photodarkening. The photodarkening is considered to be due to trapped electrons in glass matrix [3,4] or photoinduced traps, which act as nonradiative recombination centers [5,6]. Here, we report the characteristics of photoinduced centers in CdS-doped glasses using electron spin resonance (ESR) and time-resolved luminescence spectra.

Experimental Procedure

The samples investigated were CdS-doped commercial filter glasses, Toshiba Y-45 etc., with thickness of about 2.5 mm. These glasses were exposed to pulsed light from an N_2 laser (NDC JS-1000L; wavelength = 337.1 nm, pulse duration = 5 ns, peak intensity = 4 MW/cm^2, repetition rate = 4 Hz) at 300 K for 20 min. The penetration depth of N_2 laser light is less than 0.2 mm.

Transient characteristics of luminescence were measured using the following apparatus at 300 K. The excitation source was an N_2 laser (Laser Photonics LN120; wavelength = 337.1 nm, pulse duration = 0.3 ns, repetition rate = 7 Hz). The laser beam was set at an angle of about 30° off the normal incidence to the surface of the sample and was focused on an area of about 1 mm^2 by a quartz lens (focal length f = 150 mm, diameter d= 40 mm).

Since the peak intensity of the laser light is low (50 kW/cm^2), photodarkening effects were not observed at this intensity. Luminescence was collected normal to the sample surface, focused on the end of an optical fiber by a quartz lens (f = 50.8 mm), and then led to a 27 cm monochromator (Jarrel-Ash Monospec 27) Time-resolved luminescence spectra were measured using an optical multichannel analyzer with gate (Princeton Instruments D/SIDA-700). The minimum gate time is 5 ns.

The ESR spectra were measured at 77 K, using an X-band spectrometer (JES FE-1X). The first derivative spectra were obtained by a 100 kHz modulation. The g-values of signals were determined using a MgO:Mn marker.

Results and Discussion

Fig. 1 shows luminescence spectrum of the CdS-doped glasses Y-45 at 300 K. Two luminescence bands are observed. One luminescence band at 440 nm is attributable to the shallow-trapping state-to-band-type transition and another band near 600 nm to the deep trapping state-to-band-type transition[7]. Spectral shape of luminescence changes slightly by laser light irradiation: relative intensity of the 600 nm band to the 440 nm band reduces slightly. On the other hand, luminescence intensity decreases by irradiation. The intensity after irradiation is less than 1/10 of that before irradiation. This result indicates that nonradiative recombination centers are created by light irradiation. These centers open an additional channel for recombination of excited carriers, so that the decay rate of luminescence may increase. The inset in Fig. 1 shows luminescence intensities at 440 nm as a function of time at 300 K. Intensities at t = 0 ns are normalized. The initial decay rate of the 440 nm band increases after irradiation. Although the decay rate does not recover its initial value after annealing at 200 °C for 15 min, it recovers after annealing at 400 °C for 2 h.

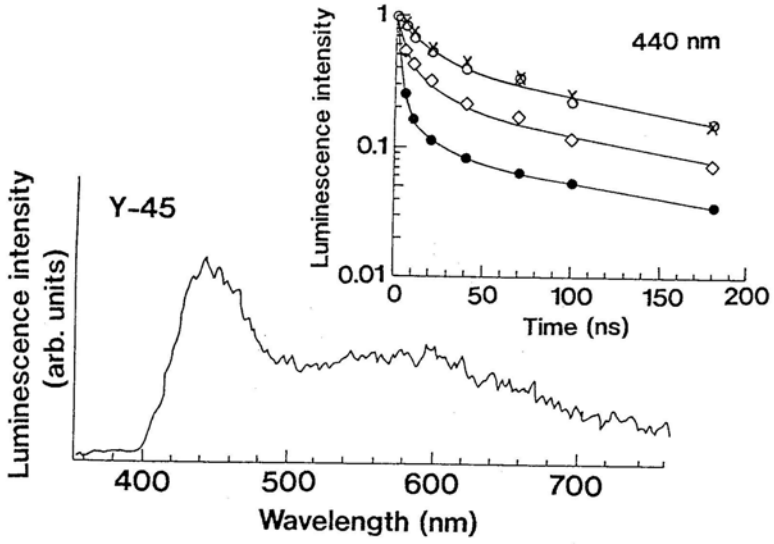

Fig. 1 Luminescence spectrum of CdS-doped glass at 300 K. The inset shows luminescence intensities at 440 nm as a function of time: before irradiation (open circles), after irradiation (solid circles), after annealing at 200 °C (squares) and after annealing at 400 °C (crosses). Solid curves were drawn through data points as guide to the eyes. Intensities at t = 0 ns are normalized.

Fig. 2 shows ESR spectra of Y–45 at 77K. The ESR signals appear by light irradiation. The ESR signals C and D disappear after annealing at 200 °C for 15 min, and signals A and B almost disappear after annealing at 400 °C for 2 h. Correlation was observed between the decay rate of luminescence and the intensity of ESR signals A and B.

Fig. 3 shows intensity of ESR signal B as a function of irradiation time for laser intensity of about 1 MW/cm^2. The ESR signal is proportional to irradiation time when shorter than about 50 s. This signal saturates for irradiation time longer than about 50 s. The decay rate of luminescence also shows saturation as shown in Fig. 3. These correlations between the intensity of the ESR signal B and decay rate of luminescence suggest that the centers responsible for the ESR signal B are associated with photodarkening effects.

We measured ESR spectra of bare fine particles of CdS, however, photoinduced signal was not observed. On the other hand, we observed photoinduced signal in glass, which does not contain CdS microcrystals, after KrF laser light (wavelength = 248 nm) irradiation[8]. This signal is attributable to photoinduced centers in glass. However, this signal disappears after annealing at 200 °C. These results suggest that the photoinduced defects in CdS–doped glass are created in the interface region between CdS microcrystals and the glass matrix.

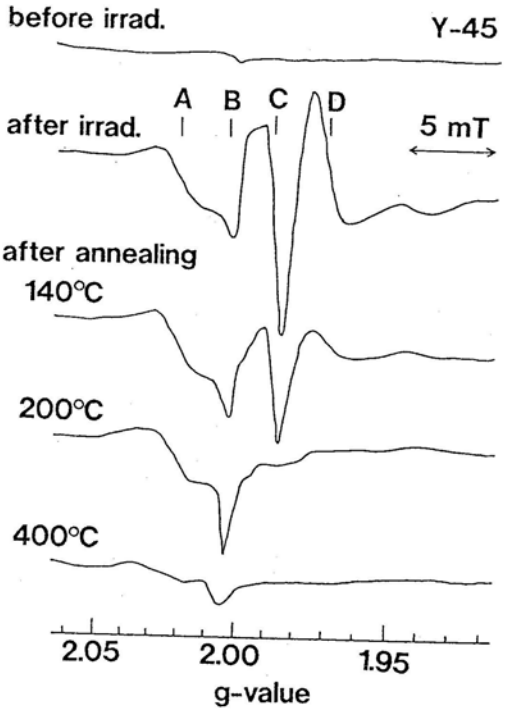

Fig. 2 ESR spectra of CdS–doped glass at 77K.

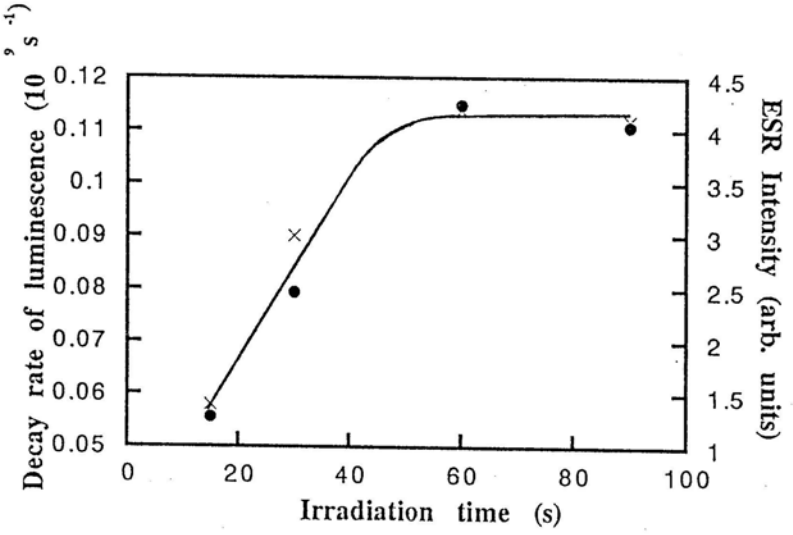

Fig. 3 Intensity of ESR signal B (crosses) and decay rate of luminescence (solid circles) of CdS–doped glass Y–45 as a function of irradiation time. Solid curve was drawn through data points as guide to the eyes.

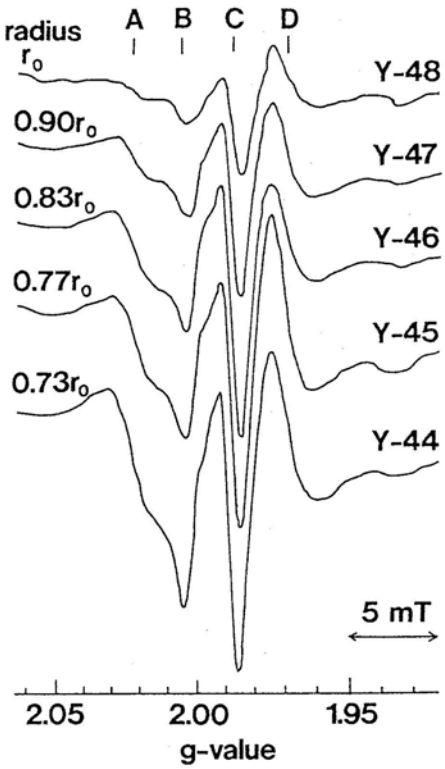

Fig. 4 ESR spectra of CdS-doped glasses at 77 K after light irradiation.

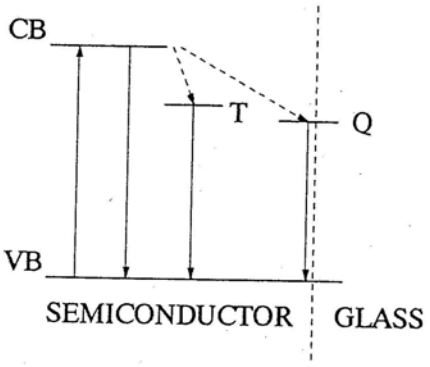

Fig. 5 Model for photodarkening. VB: valence band, CB: conduction band, T: traps, Q: photoinduced centers.

Intensity of ESR signal B as a function of size of microcrystals was measured[9]. Fig. 4 shows the ESR spectra of light-irradiated CdS-doped glasses at 77 K. Radius r of CdS microcrystals is smaller for Y-44 and larger for Y-48. Since all the glasses contain the same volume of semiconductor phase, the product of number density of microcrystals and the volume of one microcrystal is constant. Thus number density of microcrystals is proportional to r^{-3}. Since the surface area of microcrystals is proportional to r^2, the sum of the surface area of all microcrystals in the glass is proportional to r^{-1}. The ESR signal B is proportional to r^{-1}. Thus the result indicates that the signal B is associated with the photoinduced centers at the glass-semiconductor interface.

Fig. 5 shows model for photodarkening. Under laser irradiation, centers Q are created in the interface region between CdS microcrystals and the glass matrix. Centers Q act as nonradiative recombination centers, so that luminescence intensity decreases and decay rate of luminescence increases.

We also investigated commercial filter glasses from other manufacturer: Hoya. Glass composition of Hoya filter is different from that of Toshiba filter as shown in Table 1[10].

Table 1. Glass composition [wt %]. Values are from ref. 10.

	SiO_2	Na_2O	K_2O	ZnO	B_2O_3
Toshiba	67.2	13.3	5.7	9.3	3.3
Hoya	49.0	3.8	19.1	19.1	3.6

Fig. 6 shows ESR spectra of Hoya Y–46. Since Y–45 is not produced by Hoya, we measured Y–46. ESR signal was observed in unirradiated sample. This signal does not disappear by annealing at 400 °C. ESR spectrum after light irradiation is similar to that of Toshiba filter Y–45. Size dependence of ESR signal was also measured for Hoya filter and found to be similar to that of Toshiba filter glasses. We also measured ESR spectrum of Hoya glass which does not contain CdS microcrystals. The spectrum is similar to that of Toshiba. Since ESR spectra of Hoya glasses after irradiation are similar to those of Toshiba glasses, we consider that the photoinduced defects in Hoya samples have the same origin as those in the Toshiba samples.

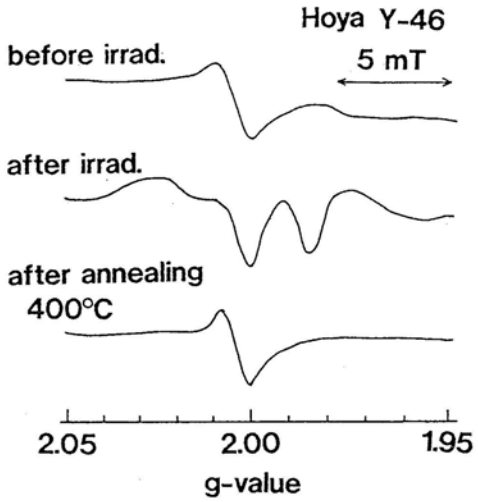

Fig. 6 ESR spectra of Hoya filter glass at 77 K.

Summary

Luminescence and ESR of CdS–doped glasses are measured. Photoinduced ESR signals were observed. The correlation between the ESR signals and the decay rate of luminescence indicates that the photoinduced centers responsible for the ESR signal are associated with photodarkening. The photoinduced centers are created in the interface region between CdS microcrystals and glass matrix.

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