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Effects of glass composition on photodarkening in CdS-doped glasses

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Photodarkening was investigated in CdS-doped glasses using luminescence and electron spin resonance (ESR). Photodarkening depends on manufacturers of glasses. The main origin of the difference in photodarkening is attributable to the difference in glass composition. © *1999 Kluwer Academic Publishers*

1. Introduction

The optical properties of semiconductor-doped glasses have been studied extensively. Photoinduced changes in the optical properties are observed and are called photodarkening [1]. Differences in the photodarkening between samples from different manufacturers have been reported by Horiuchi and Uesu [2] and Yanagawa *et al*. [3]. However, they used glasses doped with CdS_xSe_{1-x}, which are alloy semiconductors, so that not only glass composition but also chemical composition of alloy semiconductors differ. Glass samples from different manufacturers show different composition of semiconductors, even if the glasses show almost the same optical transmission spectra. For example, Toshiba O-56, Hoya O-56, Schott OG-570 and Corning 3-66 show almost the same optical transmission spectra (Horiuchi and Uesu [2] used these glasses). However, the composition x of CdS_xSe_{1-x} nanocrystals determined from Raman spectra depends on the manufacturer: $x = 0.23$ (Toshiba), 0.26 (Hoya), 0.60 (Schott) and 0.64 (Corning) [4]. In this paper, we used glasses doped with CdS nanocrystals to investigate the dependence on glass composition only. We measured time-resolved luminescence spectra and electron spin resonance (ESR) spectra of glasses from different manufacturers.

2. Experimental procedure

The samples investigated were commercial CdS-doped filter glasses whose absorption edge is near 440 nm from different manufacturers: Toshiba, Hoya, Schott and Corning. The size of samples were $2.5 \times 2.5 \times 25$ mm^3. These glasses were exposed to pulsed light from an N_2 laser (Usho YKN-900; wavelength = 337.1 nm, pulse duration = 5 ns, peak intensity = 4 MW/cm^2, repetition rate = 1 Hz) at 300 K for 5 min in each 6 points for both sides. The laser beam was focused on an area of about 4 mm^2 by a quartz lens. The penetration depth of the N_2 laser light was estimated from optical transmittance of the glasses. The penetration depth is less than 0.2 mm.

Time-resolved luminescence spectra were measured using the following apparatus at 300 K. The excitation source was another 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 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). The peak intensity of the laser light is about 50 kW/cm^2 (photodarkening was not observed at this intensity). Luminescence from the sample was collected by a quartz lens ($f = 50.8$ mm), focused on an end of an optical fiber, and then led to the slit of a spectrometer. Time-resolved luminescence spectra were measured using an optical multichannel analyzer with gate (Princeton Instruments D/SIDA-700). The minimum gate time was 5 ns. The ESR spectra were measured at 77 K using an X-band spectrometer (JES FE-1X). The g-value of the signal were determined using a MgO:Mn marker. The glass composition was analyzed by an electron probe microanalyzer (EPMA; Kevex Delta II) at an acceleration voltage of 15 kV.

3. Results and discussion

Fig. 1 shows the luminescence spectra of CdS-doped glasses before and after laser light irradiation at 300 K. The luminescence band at about 440 nm is attributable to the band-to-band or shallow-trapping state-to-band transition and another band at about 600 nm to the deep-trapping state-to-band transition [5]. For each sample, the luminescence intensity after irradiation is smaller than that before irradiation. The change in luminescence intensity near 440 nm is least for Corning 3-73, and is largest for Toshiba Y-44. The intensity after irradiation is about 1/10 of that before irradiation for Toshiba Y-44. These results are similar to those reported by Horiuchi and Uesu [2]. They measured

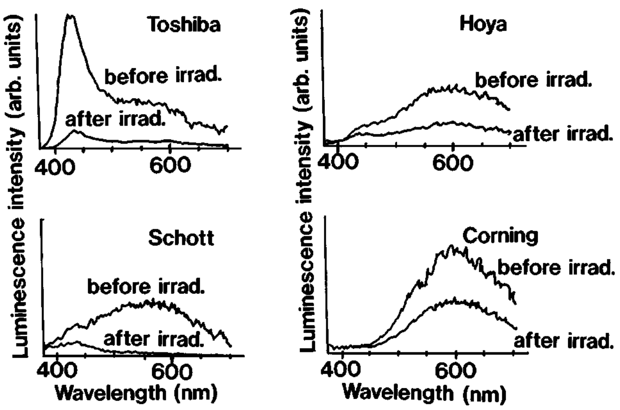

Figure 1 Luminescence spectra of CdS-doped glasses before and after laser light irradiation at 300 K: Toshiba Y-44, Hoya Y-44, Schott GG-435 and Corning 3-73.

the third-order nonlinear susceptibility and photoluminescence spectra of CdS_xSe_{1-x}-doped glasses: Toshiba O-56, Hoya O-56, Schott OG-570 and Corning 3-66. They observed a large photoinduced change for the Toshiba and Hoya glasses and a small change for Schott and Corning glasses. The compositions x of the semiconductor nanocrystals in these glasses are described in Section 1.

Fig. 2 shows the decay rate of luminescence at about 440 nm. The decay rate of luminescence changes after irradiation. We also measured the decay rate of luminescence from glasses annealed at 200 °C for 30 min, and 400 °C for 2 h after irradiation. Although the decay rate of luminescence does not recover its initial value after annealing at 200 °C, it almost recovers after anealing at 400 °C. The decay rate of luminescence at about 600 nm also shows similar behavior. The change in the decay rate caused by light irradiation differs between samples from different manufacturers. These results are similar to those reported by Yanagawa *et al.* [3]. They measured the time response of degenerate four-wave mixing signal of CdS_xSe_{1-x}-doped glasses: Toshiba R-66, Hoya R-66, Schott RG-665 and Corning 2-64. They observed a large change in the time response for Toshiba and Hoya glasses, a small change for the Schott glass and a negligible change for the Corning glass. It is difficult to determine x for the nanocrystals in these glasses from Raman spectra, since the CdS-like mode is very weak. While the CdS-like mode is observed for the Corning glass, this mode is hardly observed in the other glasses. Thus the composition x for the Corning glass is larger than those for the other glasses studied by Yanagawa *et al.* [3].

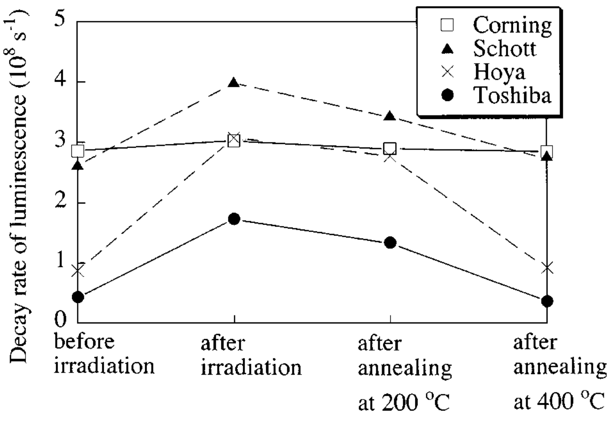

Figure 2 Decay rate of Luminescence of CdS-doped glasses (Toshiba Y-44, Hoya Y-44, Schott GG-435 and Corning 3-73) before light irradiation, after irradiation, after annealing at 200 and 400 °C.

TABLE I Composition of glasses: Toshiba Y-44, Hoya Y-44, Schott GG-435 and Corning 3-73

Sample	SiO_2	Na_2O	K_2O	ZnO	Sb_2O_3	Al_2O_3
Toshiba	78.5	1.1	13.2	1.2	4.8	1.2
Hoya	78.2	1.4	15.0	1.5	0.0	3.9
Schott	65.9	3.9	15.5	6.3	5.8	2.6
Corning	87.1	2.9	2.3	3.6	0.9	3.2

The present results indicate that the difference in glass composition is the primary origin of the difference in photodarkening between samples from different manufacturers. Although photodarkening in CdS_xSe_{1-x}-doped glasses with larger x (Corning) is less than that with smaller x (Toshiba and Hoya) [2, 3], the difference in composition x of semiconductor nanocrystals probably plays only a secondary role even in these glasses.

Since CdS-doped glasses contain ZnO (Table I), we considered possibility of formation of ZnS-CdS solid solution. The solid solution is formed by heat treatment at high temperature and for long time (700 °C for 0.5 h or 600 °C for 16 h) [6]. Size of CdS nanocystals formed at these conditions is large, and absorption edge is located at longer wavelength. However, samples investigated were formed at not so high temperature and not so long time, since size of nanocystals should be small in these samples. If the solid solution is formed, absorption spectrum shows significant steepening [6]. However, such steepening was not observed. Thus the solid solution is probably not formed.

Photodarkening depends on size of CdS nanocrystals, and it occurs easily in samples with small size CdS nanocrystals [7]. Since four samples show the same absorption edge (same quantum size effect), they are considered to contain the same size of CdS nanocrystals.

Figs 3–6 show the ESR spectra of CdS-doped glasses at 77 K before and after light irradiation. The intensity of the signal near $g = 2.01$, which is associated with photodarkening [8], increases after light irradiation. The largest change is observed for the glass Toshiba Y-44, the second for Hoya Y-44, and the third for Schott GG-435. The smallest one is for Corning 3-73. The intensity of the signal near $g = 2.01$ is correlated with the change in the decay rate of luminescence. Change in the decay rate is largest for Toshiba Y-44, the second for Hoya Y-44 and the third for Schott GG-435. The smallest one is for Corning 3-73. We also observed a similar trend in the glasses: Toshiba L-42, Hoya L-42, Schott GG-420 and Corning 3-74.

The ESR signal near $g = 2.01$ is considered to be due to photoinduced defect centers in the interface region

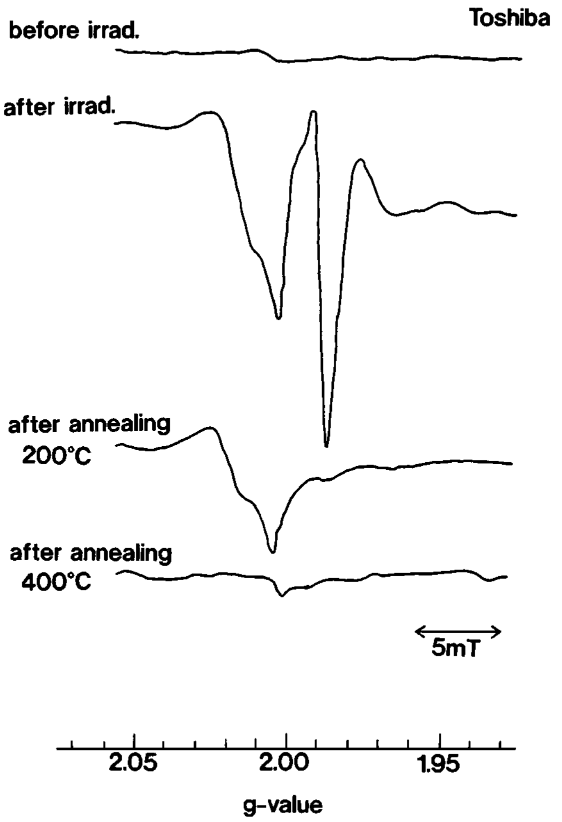

Figure 3 ESR spectra of Toshiba Y-44 at 77 K.

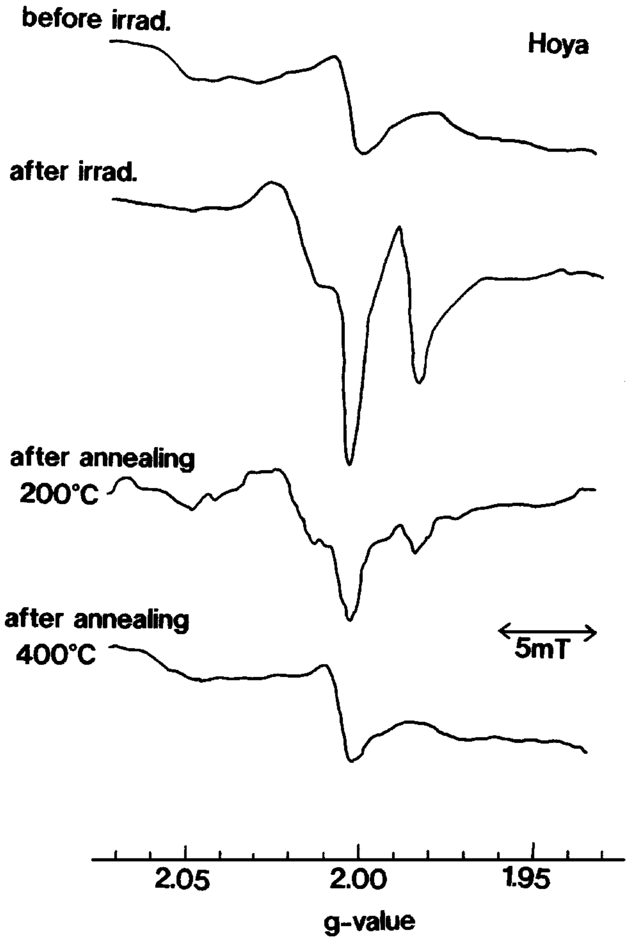

Figure 4 ESR spectra of Hoya Y-44 at 77 K.

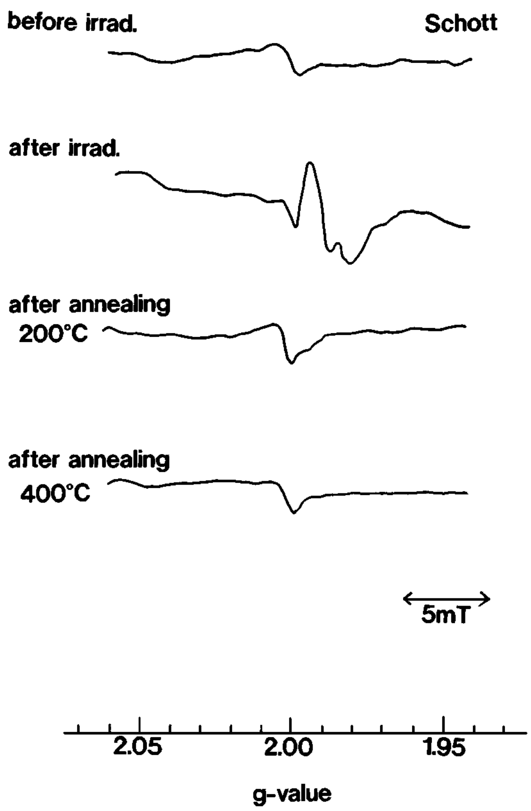

Figure 5 ESR spectra of Schott GG-435 at 77 K.

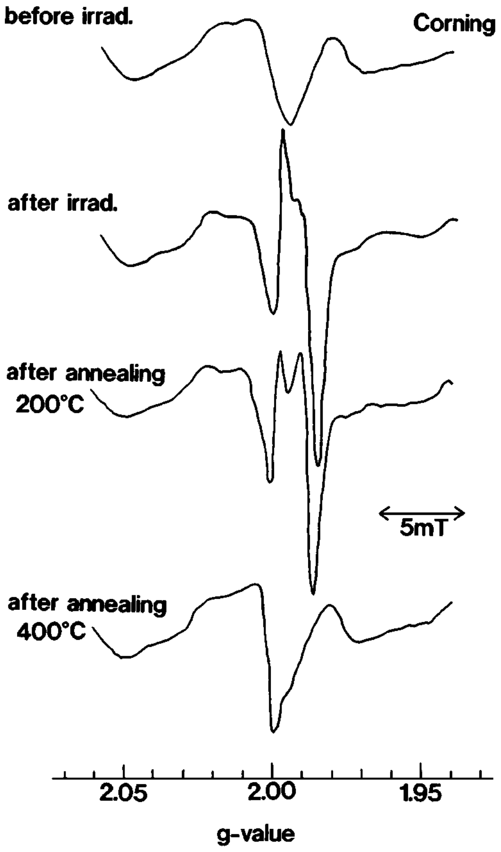

Figure 6 ESR spectra of Corning 3-73 at 77 K.

between CdS nanocrystals and glass matrix [8]. These centers act as nonradiative recombination centers and provide additional channels for the recombination of excited carriers, therefore the decay rate of the luminescence is increased. From the ESR spectra, we consider that Corning 3-73 has many defect centers before light irradiation, since a large ESR signal is observed before irradiation. Figs 3–6 also show ESR spectra of samples annealed at 200 °C for 30 min, and at 400 °C for 2 h after irradiation. An ESR signal at about $g = 1.99$ appears after light irradiation. This signal disappears after annealing at 200 °C for Toshiba Y-44 and Schott GG-435, decreases for Hoya Y-44, and does not change for Corning 3-73. The intensity of the signal near $g = 1.99$ is not correlated with the change in the decay rate of luminescence, since the change in the decay rate is slight after annealing at 200 °C. The signal at about $g = 1.99$ is considered to be due to electron traps in the glass. The ESR spectra recover their initial shape after annealing at 400 °C except for Corning 3-73. The effect of annealing on the ESR signal near $g = 2.01$ is correlated with the effect on luminescence. Luminescence properties recover their initial values after annealing at 400 °C as shown in Fig. 2.

The decay rate of luminescence and ESR spectra differ between samples. The main origin of these differences is attributable to the difference in glass composition. Table I shows the glass composition for each sample. These glasses must contain B_2O_3. However this oxide is not detected by the EPMA, since boron is a light element. Although data are not corrected, qualitative comparison is possible for other oxides. The quantity of K_2O in Corning 3-73 is less than those in other glasses. Similar results have been reported by Yanagawa *et al.* [3]. They measured glass composition using X-ray fluorescence and wet chemical method. They found that K_2O was not contained in the glass of Corning. Therefore, they concluded that K^+ ions played a key role in the photodarkening. However, further investigation is necessary to reach a firm conclusion.

4. Summary

We measured time-resolved luminescence spectra and ESR spectra before and after light irradiation for four colored filter glasses. The changes in the decay rate of luminescence and in the intensity of ESR signal before and after irradiation are largest for Toshiba Y-44, second for Hoya Y-44 and third for Schott GG-435. These hardly occur for Corning 3-73. These results are similar to those reported by Horiuchi and Uesu [2] and Yanagawa *et al*. [3]. The main origin of the difference in photodarkening is attributable to the difference in glass composition.

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