

Dependence of Photodarkening on Alloy Composition of $\text{CdS}_x\text{Se}_{1-x}$ Nanocrystals in Glasses

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(Received March 23, 1998; accepted May 29, 1998)

Photodarkening has been investigated in $\text{CdS}_x\text{Se}_{1-x}$ -doped glasses using luminescence and electron spin resonance (ESR). Photodarkening does not occur when the wavelength of the laser light is longer than 640 nm, even if the laser light is absorbed by glasses. This result is explained by the two-step excitation process.

KEYWORDS: semiconductor, nanocrystal, quantum dot, photodarkening, luminescence, ESR

The optical properties of semiconductor nanocrystals in glasses (CdS-, CdSSe- and CuCl-doped glasses) have been investigated extensively, since these materials have large optical nonlinearity with a fast response time.¹⁾ Roussignol *et al.*²⁾ reported that the response time of nonlinear signals and luminescence of CdS_xSe_{1-x}-doped glass decreased with light irradiation. This photoinduced irreversible process is called photodarkening. A two-step excitation process for photodarkening was proposed by Malhotra *et al.*³⁾ and modified by Miyoshi *et al.*⁴⁾ Electrons in the valence band of semiconductor nanocrystals are excited to the conduction band (first step), some of which relax into traps at the glass-semiconductor interface. Before the electrons recombine, laser light reexcites some of these trapped electrons to higher-energy surface states (second step), from which they migrate into the glass. These electrons eventually relax to deep levels in the glass. Photogenerated holes in CdS nanocrystals migrate into the interface region between CdS nanocrystals and the glass matrix, and activate defect centers. These defect centers may act as nonradiative recombination centers, and photodarkening is considered to be related to the defect centers.

The photon energy required for the first step decreases in CdS_xSe_{1-x}-doped glass with decreasing sulphur fraction, x , since the band gap energy of CdS_xSe_{1-x} nanocrystals decreases. If the photon energy required for the second step does not change to a significant extent with decreasing x , the second step excitation may not occur, when the CdS_xSe_{1-x}-doped glass with a small value of x is exposed to light with the critical wavelength, whose photon energy corresponds to the band gap energy of CdS_xSe_{1-x} nanocrystals. Here, we report the dependence of photodarkening on the alloy composition of CdS_xSe_{1-x} nanocrystals in the glasses, and the wavelength of the laser light, to ascertain the validity of the two-step excitation process.

The samples investigated were CdS_xSe_{1-x}-doped commercial filter glasses (Hoya Y-50, Y-52, O-54, O-56, O-58, R-60, R-62, R-64, R-66 and R-68) of about 2.5 mm thickness. The concentration of CdS_xSe_{1-x} was about 0.5 wt%. The alloy compositions of CdS_xSe_{1-x} nanocrystals were determined by their Raman spectra.⁵⁾ These 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 =

5 MW/cm²) for 2 min, or a tunable laser (Quanta-Ray MOPO-700; pulse duration = 5 ns, repetition rate = 11 Hz, peak power density = 10 MW/cm²) for 4 min, 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/cm², repetition rate = 4 MHz). The decay time of the luminescence was measured 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.

When the Ti:sapphire laser was used as the excitation source, we observed a luminescence band at about 500 nm in Y-50, 520 nm in Y-52 and 540 nm in O-54. This band is attributable to the band-to-band type, or shallow trapping state-to-band-type transition.⁶⁾ Luminescence intensity decreases after irradiation, as do the transient characteristics of luminescence. Since luminescence intensity decays nonexponentially,⁷⁾ we use the intensity ratio, $I(0.1)/I(0)$, as the measure of decay time, where $I(0)$ is luminescence intensity at $t = 0$ ns (zero time delay) and $I(0.1)$ is that at $t = 0.1$ ns. Figure 1 shows the decay times of luminescence from CdS_{*x*}Se_{1-*x*}-doped glasses, from Y-50 to R-68, at peak wavelengths; the open circles show the decay times of luminescence from samples before irradiation, and the solid triangles show those after irradiation of light with the critical wavelengths, i.e., 500 nm for Y-50, 520 nm for Y-52, 540 nm for O-54. The optical transmittance of the sample at the critical wavelength is about 50%, and the transmittance decreases with decreasing light wavelength. The solid squares show decay times of luminescence from samples after irradiation of 355 nm light. The decay times of luminescence from samples after irradiation of 355 nm light are shorter than those after irradiation of light with the critical wavelength. Since the penetration depth of 355 nm light is shallow (less than 0.1 mm), the density of the defect centers is high at the surface region of the glass. On the other hand, the penetration depth of light with the critical wavelength is deep (more than 2.5 mm), since optical transmittance at this wavelength is about 50%. Thus, the density of the defect centers at the surface region is lower than that after irradiation of 355 nm light. Since the wavelength of laser light for luminescence measurements is short

Fig.1

(390 nm), we observe luminescence from the surface region of the glasses. Although the decay times of luminescence from glasses after irradiation of 355 nm light are shorter than those before irradiation for all glasses, it should be noted that the changes in decay times for R-64, R-66 and R-68 were very small when they were exposed to light with the critical wavelength. Fig.2

We measured the luminescence decay times of R-68 as a function of the wavelength of the laser light used for irradiation; Fig. 2 shows the results. The change in decay times is small for laser light with wavelengths longer than 640 nm.

These results are explained by the two-step excitation process.^{3,4)} Electrons in the valence band are excited to the conduction band (first step), some of which relax into traps. Laser light reexcites some of these trapped electrons to higher-energy surface states (second step), from which they migrate, and relax to deep levels in the glass. When the wavelength of the laser light is longer than 640 nm, the second step does not occur, since the photon energy is too low to excite electrons. Defect centers are not activated in this condition. Thus, photodarkening does not occur.

We measured ESR spectra to validate the hypothesis described above. In CdS- and CdS_xSe_{1-x}-doped glasses, ESR signals appear after irradiation.^{4,8,9)} The ESR signal at approximately $g = 1.99$ is considered to originate from the electrons trapped in the glass, and that at approximately $g = 2.01$, from the photoinduced defect centers in the interface region between the semiconductor nanocrystals and the glass matrix. Since the intensity of the ESR signal at approximately $g = 2.01$ is weak and overlaps the other signal in CdS_xSe_{1-x}-doped glasses, we use the ESR signal at approximately $g = 1.99$ as a measure of photodarkening. Figure 3 shows the intensities of the ESR signals in CdS_xSe_{1-x}-doped glasses, from Y-50 to R-68, at 77 K; these glasses were exposed to light with the critical wavelength. The signal intensity is very weak for R-64, R-66 and R-68, where light with wavelengths of 640 nm, 660 nm and 680 nm, respectively, were used. This result supports the assumption of the two-step excitation process, and indicates that photodarkening does not occur when glasses are exposed to light with wavelength longer than 640 nm. Fig.3

In summary, the luminescence and ESR spectra of CdS_xSe_{1-x}-doped glasses were measured before and after laser irradiation. Photodarkening is observed after irradiation of

laser light with short wavelengths. However, photodarkening is not observed when the wavelength of the laser light is longer than 640 nm, even if the laser light is absorbed by glasses. This result is explained by the two-step excitation process.

This work was performed using the ESR spectrometer in the laboratory of Professor T. Miki, and lasers in the Venture Business Laboratory, Yamaguchi University. The authors are grateful to Professor T. Miki and Associate Professor K. Kasatani.

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Figure captions

Fig. 1. Decay times of luminescence from $\text{CdS}_x\text{Se}_{1-x}$ -doped glasses, from Y-50 to R-68, at peak wavelengths, at 300 K. Curves were drawn through the data points as a guide for the eyes.

Fig. 2. Luminescence decay time of $\text{CdS}_x\text{Se}_{1-x}$ -doped glass, R-68, as a function of wavelength of the laser light used for irradiation. A curve was drawn through the data points as a guide for the eyes.

Fig. 3. ESR intensities of $\text{CdS}_x\text{Se}_{1-x}$ -doped glasses, from Y-50 to R-68, after irradiation. A curve was drawn through the data points as a guide for the eyes.

Fig. 1

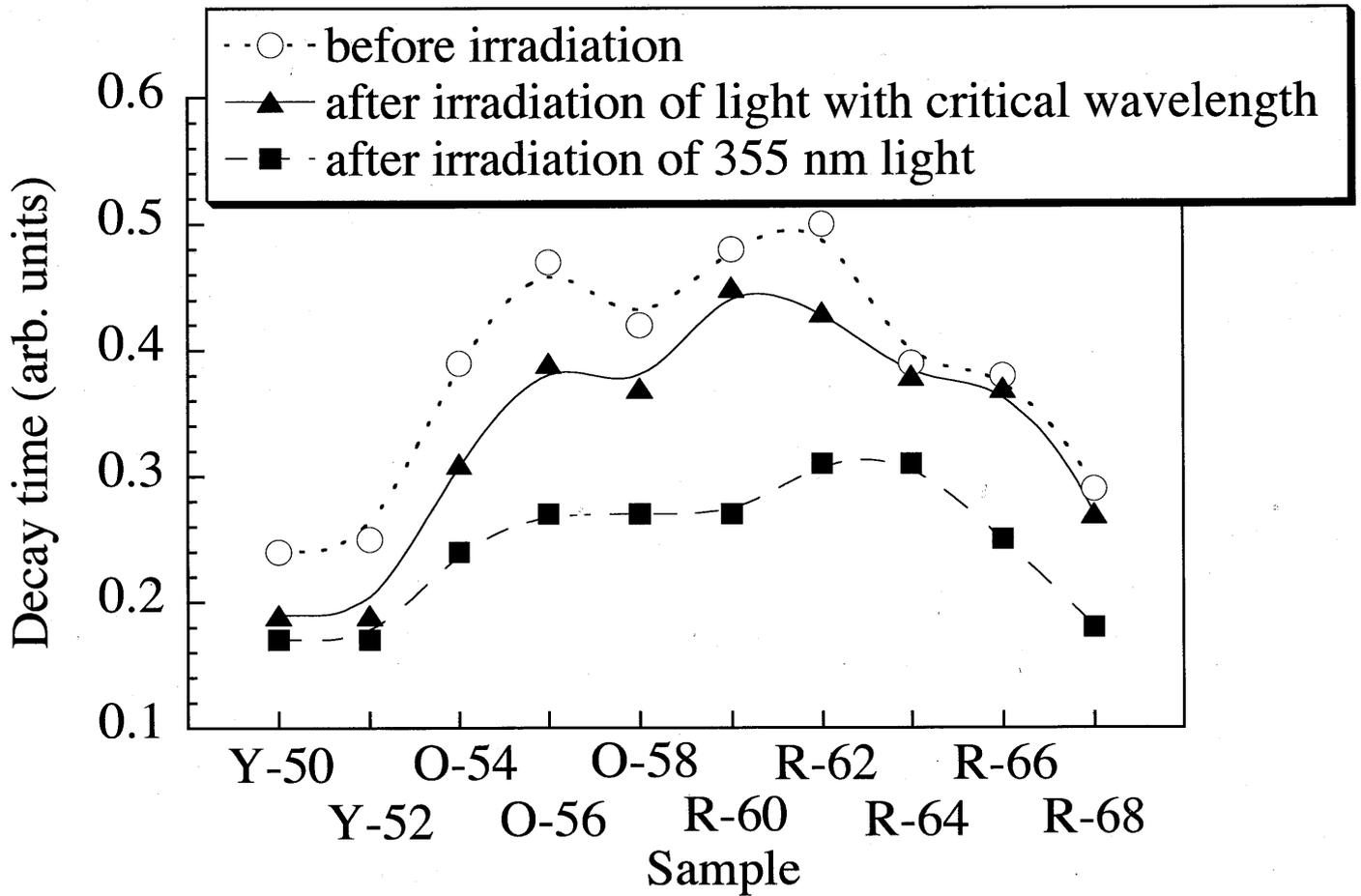


Fig. 2

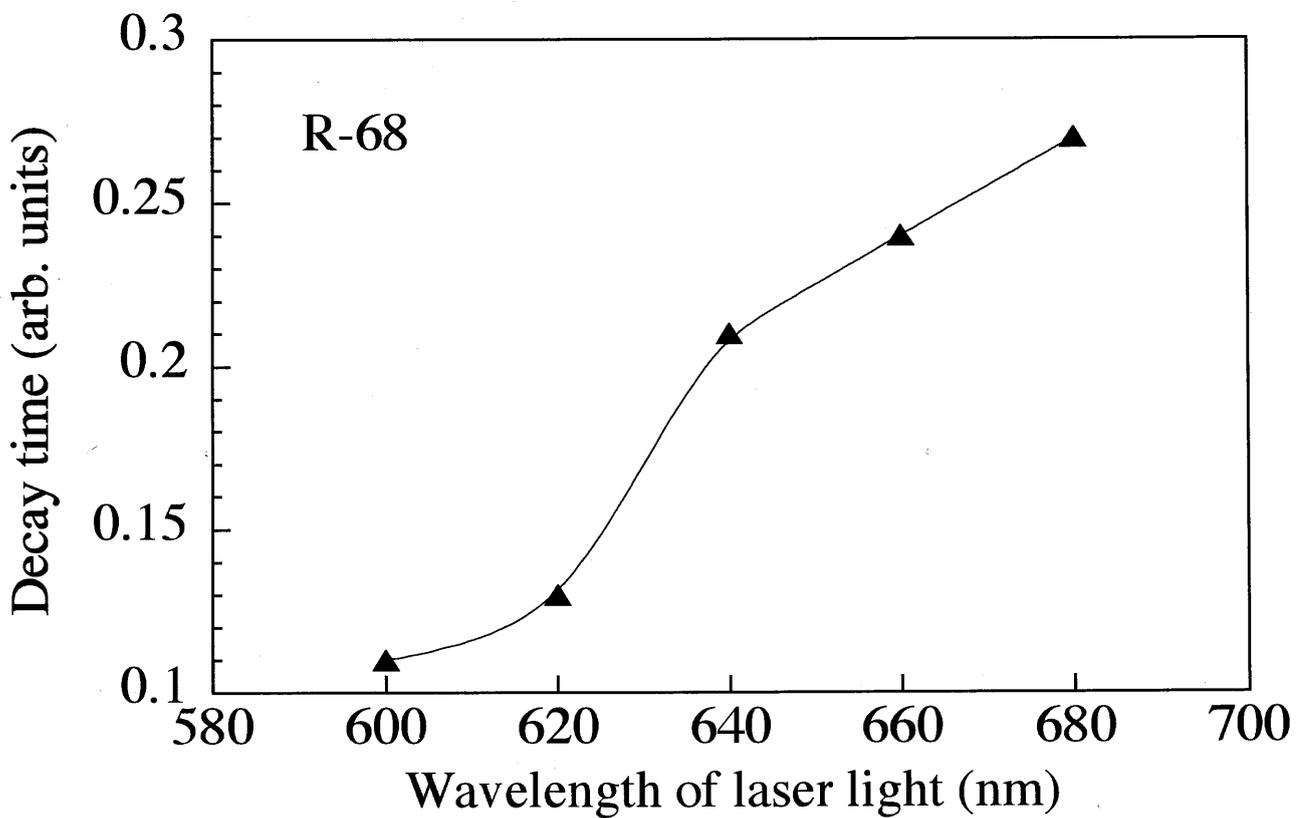


Fig. 3

