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Photoinduced Formation of CdSSe Nanocrystals in Glass

Tadaki Miyoshi, Hirofumi Fukuda and Naoto Matsuo

Department of Electrical and Electronic Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755, Japan

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The optical transmission and luminescence spectra of CdSSe-doped glass before heat treatment were measured. This glass does not contain CdSSe nanocrystals. The optical transmittance decreases and luminescence intensity increases upon laser irradiation. These results indicate that the CdSSe nanocrystals are formed by laser irradiation. When the wavelength of laser light is changed, a notable change in the absorption edge of induced absorption is not observed. Transient characteristics of luminescence from the CdSSe-doped glass are compared with those from the CdSSe-doped glass after heat treatment.

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

The optical properties of semiconductor-doped glasses have been studied extensively.[1–3] Jain and Lind[1] reported for the first time that these materials have a large optical nonlinearity and a fast response time. The semiconductor-doped glasses contain nanocrystals of semiconductors such as CdS or CdS_xSe_{1-x}. Cd, S and Se are dissolved in borosilicate glass at 1300–1400°C. The glass is cooled, then the nanocrystals are formed by heat treatment at 575–750°C.[2] The size of the nanocrystals depends on the temperature and length of heat treatment. In previous papers,[4,5] we reported on the formation of CdS and CdSSe nanocrystals formed by laser irradiation instead of by heat treatment. We observed changes in luminescence, ESR (electron spin resonance) and optical transmission spectra due to the formation of the nanocrystals using a nitrogen laser (wavelength = 337.1 nm). Here, we report the dependence of the optical transmittance on intensity and wavelength of laser light in CdSSe-doped glass using a pulsed Nd:YAG laser and a tunable laser.

The sample investigated was Toshiba R-02 approximately 2.5 mm thick. This sample is semiconductor-doped glass before heat treatment. Although this sample contains CdSSe, it does not contain nanocrystals of CdSSe and does not absorb visible light. When this glass is heated, nanocrystals of CdSSe are formed, and these nanocrystals absorb visible light. Toshiba O-56 is the glass produced by heat treatment of Toshiba R-02. The concentration of CdSSe is approximately 0.4 wt%. Toshiba R-02 was exposed to pulsed light from a frequency-tripled Nd:YAG laser (Quanta-Ray GCR-230T-10; wavelength = 355 nm, pulse duration = 5 ns, energy per pulse = 15 mJ, repetition rate = 11 Hz) or a tunable laser (Quanta-Ray MOPO-700; pulse duration = 5 ns, energy per pulse = 1.5 mJ, repetition rate = 11 Hz) at 300 K before heat treatment. The diameter of the laser beam was approximately 6 mm. The penetration depth of the 355 nm light is approximately 2.5 mm. Since the beam size is large and the penetration depth is deep, the laser heating effect is negligibly small.

Optical transmission spectra were measured using a spectrophotometer (Hitachi 323) 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, energy per pulse = 0.1 nJ, repetition rate = 4 MHz). The decay rate of the luminescene was measured using a streak camera (Hamamatsu C4334). Fig. 1

Figure 1 shows optical transmission spectra of CdSSe-doped glass, R-02, before and after laser irradiation. The transmittance decreases due to laser irradiation. Decrease in the transmittance at wavelengths shorter than approximately 600 nm is primarily attributable to the absorption of light by the CdSSe nanocrystals. Although the change in transmittance is not large, the shape of the transmission spectrum near 500 nm is similar to that of glass which contains CdSSe nanocrystals. This result indicates that CdSSe nanocrystals are formed in the glass by laser irradiation. Change in the transmittance was not observed in the undoped glass, which does not contain CdSSe. The decrease in the transmittance at longer wavelengths is attributable to photodarkening.[3] Decrease in the transmittance at wavelengths shorter than approximately 400 nm is primarily attributable to the absorption of the precursor of the CdSSe nanocrystals. The precursor absorbs laser light and the nanocrystals are formed. Fig. 2

Figure 2 shows the transmittance ratio of CdSSe-doped glass, R-02, at wavelengths of 500 nm and 660 nm, T(500)/T(660), as a function of irradiation time. The change in transmittance increases with increasing the irradiation time, and then reaches saturation. When laser intensity is decreased, the time required for saturation increases in proportion to the inverse of the laser intensity. This result indicates that the time required for saturation is determined by the total number of photons, and that the formation of nanocrystals is induced by photons instead of by thermal energy. When the laser intensity is altered, a notable change in the wavelength of the absorption edge is not observed.

We measured the luminescence of R-02. The luminescence intensity increases due to laser irradiation. The luminescence intensity increases with increasing irradiation time, and then reaches saturation. This saturation behavior is similar to that of transmittance. Optical properties of CdS and CdSSe-doped glasses after heat treatment are different from those before heat treatment. The luminescence intensity decreases upon laser irradiation in these glasses after heat treatment.[3,6]

We measured the transmission spectra of R-02 in the case using the tunable laser to change the wavelength of the laser light. Although a notable change in wavelength of absorption edge is not observed, a change in absorbance is observed. Figure 3 shows the value of T(500)/T(660) of CdSSe-doped glass, R-02, as a function of the wavelength of the laser light. The smallest value of T(500)/T(660) is observed for 320 nm. Since longer wavelength light is partly absorbed by the precursor of the CdSSe nanocrystals as shown in Fig. 1, the amount of CdSSe nanocrystals produced is small. On the other hand, the penetration depth of the shorter wavelength light is shallow. Since CdSSe nanocrystals are formed in only a thin layer for shorter wavelength light, absorbance is small. Thus, the maximum absorption is observed in the intermediate wavelength near 320 nm. Light with the wavelength of 320 nm is completely absorbed by glass as shown in Fig. 1. Fig. 3

Transient characteristics of luminescence from the photoinduced CdSSe nanocrystals in R-02 are compared with those from CdSSe nanocrystals formed by heat treatment in Toshiba O-56. Figure 4 shows the transient characteristics of luminescence from these CdSSe nanocrystals. The decay rate of the luminescence from R-02 (dashed curve) is faster than that from O-56 (solid curve). This is attributable to photodarkening. The main luminescence band is attributable to the band-to-band or shallow-trapping state-to-band transition.[7] Nanocrystals are formed and defect centers are created by laser irradiation.[4] The photoinduced defect centers act as nonradiative recombination centers and provide additional channels for the recombination of excited carriers, therefore the decay rate of the luminescence from R-02 is faster than that from O-56. Laser irradiated O-56 shows a similar decay rate of luminescence as that of R-02, since the photoinduced defect centers are created by laser irradiation. Fig. 4

In summary, we measured the optical transmission and luminescence spectra of CdSSe-doped glass, which does not contain nanocrystalline CdSSe, before heat treatment. The optical transmittance decreases and the luminescence intensity increases due to laser irradiation. These results indicate that the CdSSe nanocrystals are formed by laser irradiation. When the wavelength of the laser light is changed, a notable change in the absorption edge of induced absorption is not observed. The decay rate of the luminescence emitted from the photoinduced CdSSe nanocrystals is faster than that from the CdSSe nanocrystals formed by heat treatment.

This work was conducted using lasers in the Venture Business Laboratory, Yamaguchi

University.

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Figure captions

Fig. 1. Optical transmission spectra of CdSSe-doped glass, R-02, at 300 K before and after laser irradiation. The wavelength of the laser light is 355 nm. The irradiation time is 8 min and the energy per pulse is 15 mJ.

Fig. 2. The transmittance ratio of CdSSe-doped glass, R-02, at wavelengths of 500 nm and 660 nm, T(500)/T(660), as a function of the irradiation time of laser light at 300 K. The wavelength of the laser light is 355 nm. The energy per pulse is 15 mJ (a) and 4 mJ (b). Solid curves were drawn through the data points as a visual guide.

Fig. 3. The transmittance ratio of CdSSe-doped glass, R-02, at wavelengths of 500 nm and 660 nm, T(500)/T(660), as a function of the wavelength of laser light at 300 K. The irradiation time is 2 min and the energy per pulse is 1.5 mJ. A solid curve was drawn through the data points as a visual guide.

Fig. 4. Transient characteristics of luminescence from CdSSe-doped glasses, R-02 (dashed curve) and O-56 (solid curve), at 300 K. The wavelength of the laser light is 355 nm. The irradiation time is 2 min and the energy per pulse is 15 mJ.

Fig. 1

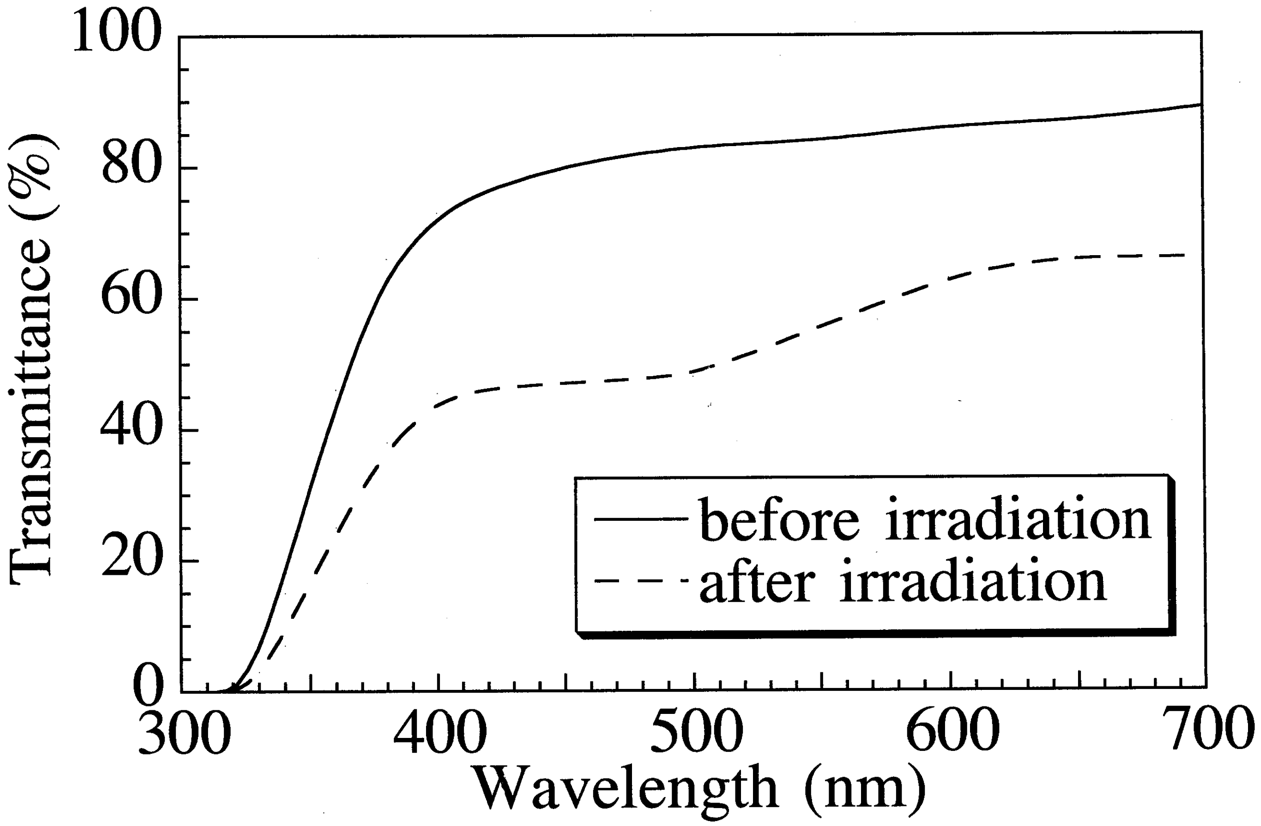


Fig. 2(a)

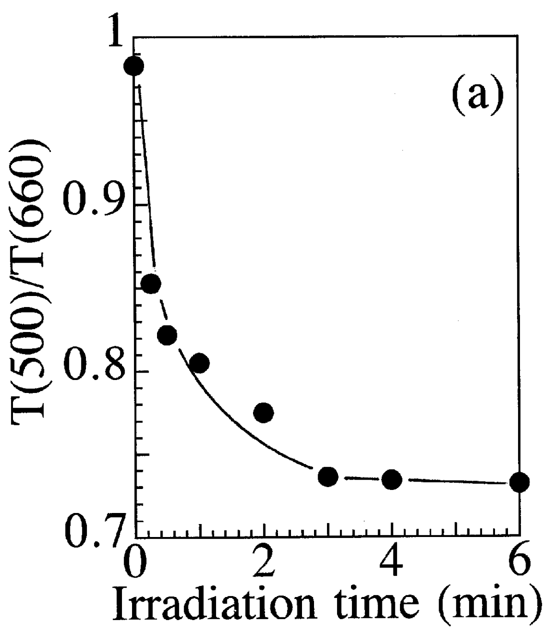


Fig. 2(b)

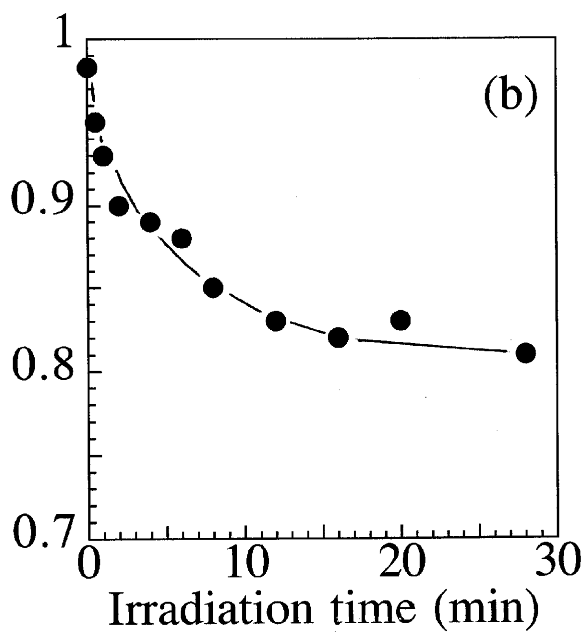


Fig. 3

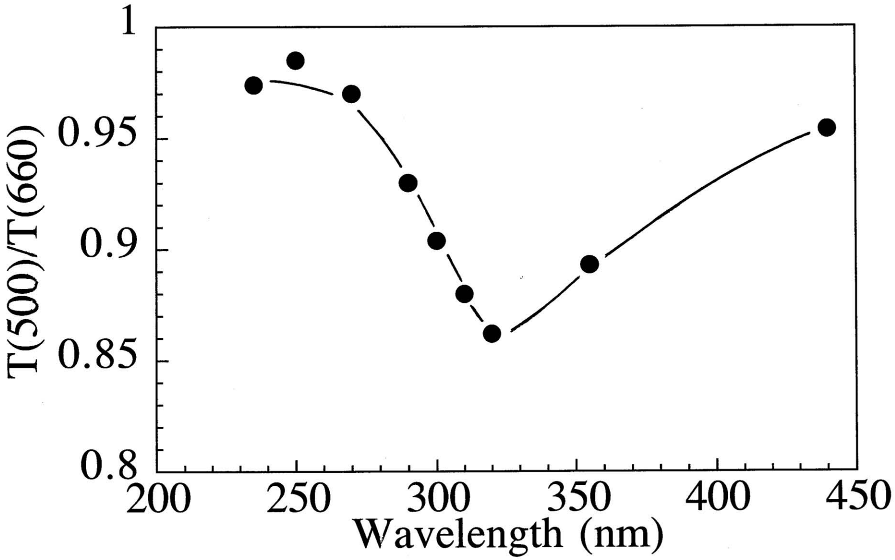
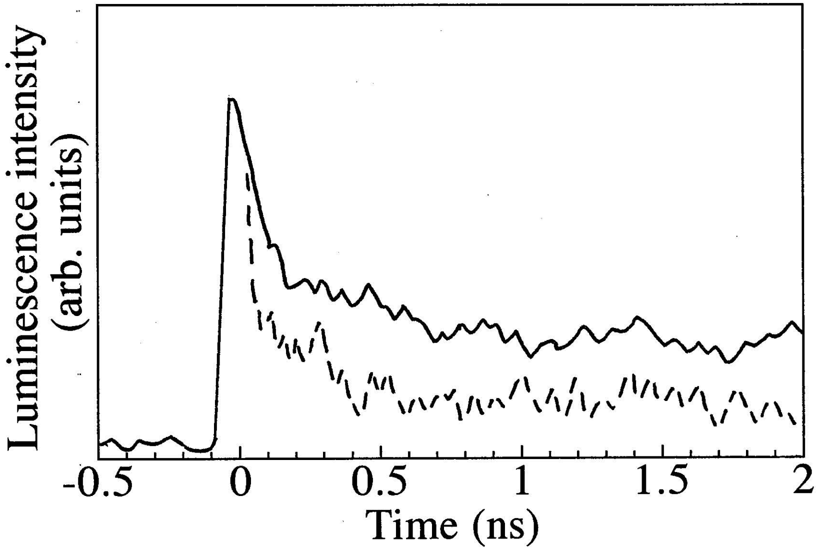

1
0.95
0.9
0.85
0.8
T(500)/T(660)
200
250
300
350
400
450
Wavelength (nm)

Fig. 4


Luminescence intensity
(arb. units)
-0.5
0
0.5
1
1.5
2
Time (ns)