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Photoinduced Formation of Semiconductor Nanocrystals in CdS-Doped Glasses

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Luminescence and electron spin resonance (ESR) of CdS-doped glass which did not contain nanocrystals of CdS were investigated. Luminescence intensity increases after laser irradiation. Luminescence and ESR spectra after laser irradiation are similar to those of CdS-doped glass which contains nanocrystals of CdS. These results indicate that the nanocrystals are formed after laser irradiation.

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

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 large optical nonlinearity with a fast response time. The semiconductor-doped glasses contain nanocrystals of semiconductors such as CdS or CdSSe. Cd, S and Se are dissolved in silicate glass at 1300–1400°C. The glass is cooled, and then the nanocrystals are formed by heat treatment at 575–750°C.[2]@ The size of the nanocrystals depends on the temperature and time of heat treatment. The optical properties of the glasses are changed by light irradiation, and these photoinduced processes are called photodarkening effects.[3] The photoinduced effects have been investigated after heat treatment of glasses which contain nanocrystals of CdS or CdSSe. However, little is known about the photoinduced effects before heat treatment of semiconductor-doped glass which does not contain nanocrystals of semiconductor. Here, we report the photoinduced effects on CdS-doped glass before heat treatment.

The samples investigated were CdS-doped commercial filter glasses (Toshiba Y-43 and Y-02) of about 2.5mm thickness. Y-43 is a filter glass obtained after heat treatment and Y-02 is that obtained before heat treatment. Concentration of CdS in 0.4 wt%. Y-43 contains nanocrystals of CdS and absorbs light with wavelength shorter than about 430 nm. In contrast, Y-02 does not contain CdS nanocrystals and does not absorb visible light. 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.

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 =337.1nm, pulse duration= 0.3 ns, repetition rate = 7 Hz). The laser beam was set at an angle of about 30° to the normal and was focused on an area of about 1mm^2 by a quartz lens (focal length f = 150 mm). Since the peak intensity of the laser light was low (50 kW/cm^2), photodarkening effects were not observed. 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 luminescene spectra were measured using an optical multichannel analyzer with a gate (Princeton Instruments D/SIDA-700). The minimum gate time was 5 ns.

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

Figure 1 shows luminescence spectra of CdS-doped glasses (Y-02 and Y-43) at 300K before and after irradiation. The shape of the luminescence spectrum of Y-43 changes slightly and the intensity of luminescence decreases upon laser irradiation. In contrast, the intensity of luminescence from Y-02 increases after irradiation. Luminescence intensity ratios are as follows: Y-43 before irradiation(1), Y-43 after irradiation(0.04), Y-02 before irradiation(0.007) and Y-02 after irradiation(0.02). The shape of the luminescence spectrum of Y-02 after irradiation is similar to that fromY-43. This result suggests that CdS nanocrystals are formed in the glass by laser irradiation. The radius of CdS nanocrystals in Y-43 is estimated to be 1.6nm according to the blue shift of the absorption edge and the calculated energy shift caused by the quantum confinement effect.[4] Fig.2

Figure 2 shows intensities of luminescence from CdS-doped glasses at peak wavelengths as a function of time at 300 K: Y-02 after laser irradiation, Y-43 before irradiation (Y-43B) and after irradiation (Y-43A). The decay rate of luminescence from Y-43 after laser irradiation is faster than that before irradiation. This result indicates that nonradiative recombination centers are created by laser irradiation. These centers provide additional channels for the recombination of excited carriers, so that the decay rate of luminescence is increased. The decay rate of luminescence from Y-02 after irradiation is faster than that from Y-43. This result indicates that the value of N_1/N_0 in Y-02 is larger than that in Y-43, where N_1 is the number of nonradiative recombination centers and N_0 is the number of nanocrystals. The weaker luminescence of Y-02 is considered to be due to the larger valus of N_1/N_0.

ESR spectra were measured to investigate the nonradiative centers. An ESR signal was not observed in CdS-doped glasses of Y-02 and Y-43 before laser irradiation. ESR signals, however, appeared after irradiation. Figure 3 shows ESR spectra of these glasses at 77 K. The signal at about $g = 2.01$ is considered to be due to photoinduced defects in the interface region between CdS nanocrystals and the glass matrix.[5,6] This result indicates that nanocrystals are formed in Y-02 and the defects are created in the glass-

semiconductor interface. The photoinduced defects are considered to act as nonradiative recombination centers, so that the decay rate of luminescence from Y-02 is fast as shown in Fig.2. Fig.3

The intensity ratio of ESR signals, $I_{2.01}/I_{1.99}$, where $I_{2.01}$ is the ESR intensity of the signal at g=2.01 and $I_{1.99}$ is that at g=1.99, depends on the size of the CdS nanocrystals. The value of $I_{2.01}/I_{1.99}$ increases with the decrease in the size of the nanocrystals. Since the value for Y-02 is larger than that for Y-43, the size of CdS nanocrystals in Y-02 is slightly smaller than that in Y-43.

The temperature rise of the glass during laser irradiation is evaluated using $Q = -KdT/dx$, where Q is the flux of thermal energy and K is the thermal conductivity of the glass. Temperature rise is estimated to be about 1°C using Q=80 mW/cm^2 (peak intensity of laser pulse = 4 MW/cm^2, pulse duration =5ns, repetition rate = 4 Hz), K =0.014W/(cm deg) and thickness of the glass = 2.5 mm. Momentary temperature rise is higher than 1°C when pulsed light from the laser is incident on the glass. However, the ESR signal at g = 1.99 disappears upon thermal annealing at 200°C,[5] implying that the temperature of the glass does not exceed 200°C. Since the temperature of the glass during laser irradiation is low, nanocrystals are considered to be formed with photon energy instead of thermal energy.

We also measured transmission spectra of Y-02 before and after laser irradiation. No change in the transmission spectrum was observed. Since the penetration depth of laser light is shallow, CdS nanocrystals may exist only in the surface region of Y-02. Thus, the change in transmittance is slight.

In summary, luminescence and ESR of CdS-doped glass which does not contain nanocrystalline CdS were measured and compared with those of CdS-doped glass which contains CdS nanocrystals. Luminescence and ESR spectra of the former glass after laser irradiation are similar to those of the latter. These results indicate that nanocrystals are formed upon laser irradiation.

References

1) R. K. Jain and R. C. Lind: J. Opt. Soc. Am. **73** (1983) 647.

2) N. F. Borrelli, D. W. Hall, H. J. Holland and D. W. Smith: J. Appl. Phys. **61** (1987) 5399.

3) R. Roussignol, D. Ricard, J. Lukasik and C. Flytzanis: J. Opt. Soc. Am. B **4** (1987) 5.

4) L. E. Brus: J. Chem. Phys. **80** (1984) 4403.

5) T. Miyoshi, K. Towata and N. Matsuo: Jpn. J. Appl. Phys.**33** (1994) 6299.

6) T. Miyoshi, H. Matsuki and N. Matsuo: Jpn. J. Appl. Phys.**34** (1995) 1837.

Figure captions

Fig. 1. Luminescence spectra of CdS-doped glasses at 300K before and after laser irradiation.

Fig. 2. Intensities of luminescence from CdS-doped glasses at peak wavelengths as a function of time at 300 K: Y-02 after laser irradiation, Y-43 before irradiation (Y-43B) and after irradiation (Y-43A).

Fig. 3. ESR spectra of CdS-doped glasses at 77K after laser irradiation.

Fig. 1

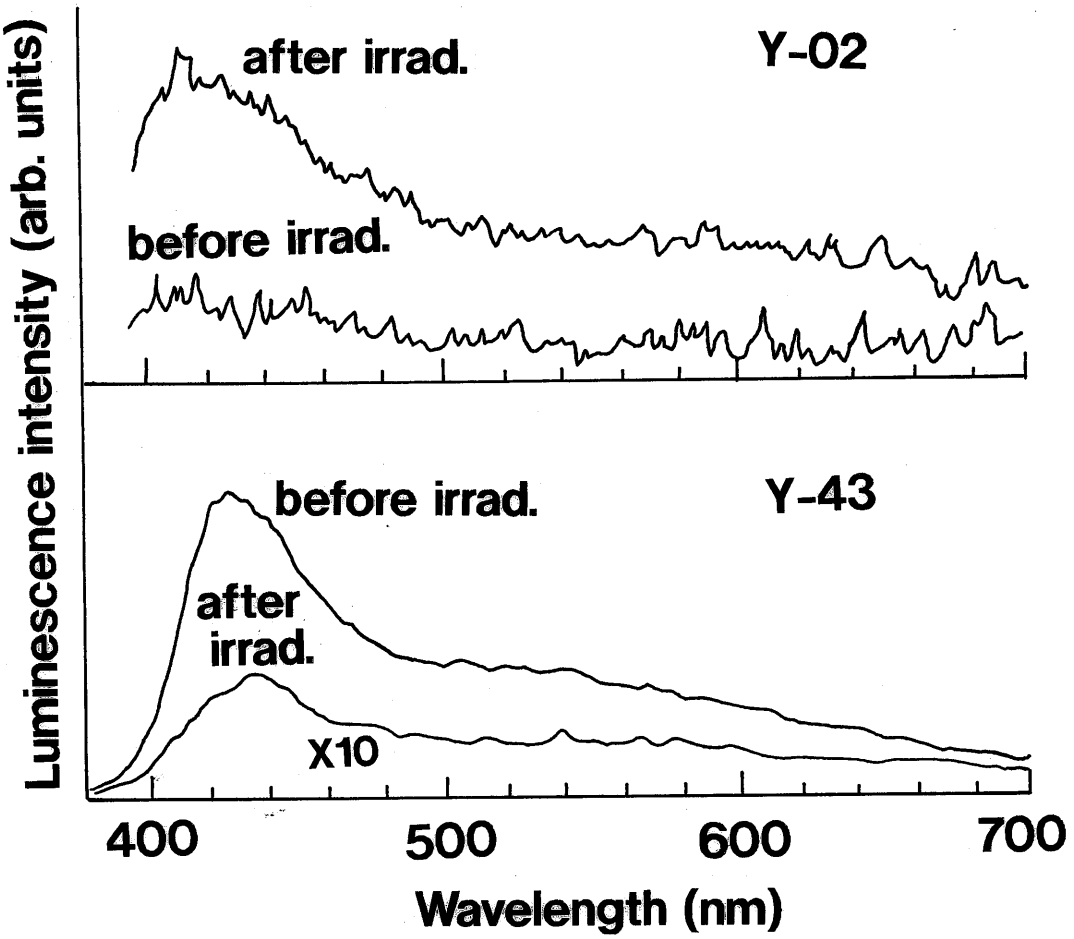
after irrad.
Y-02
before irrad.
before irrad.
Y-43
after
irrad.
X10
Luminescence intensity (arb. units)
400
500
600
700
Wavelength (nm)

Fig. 2

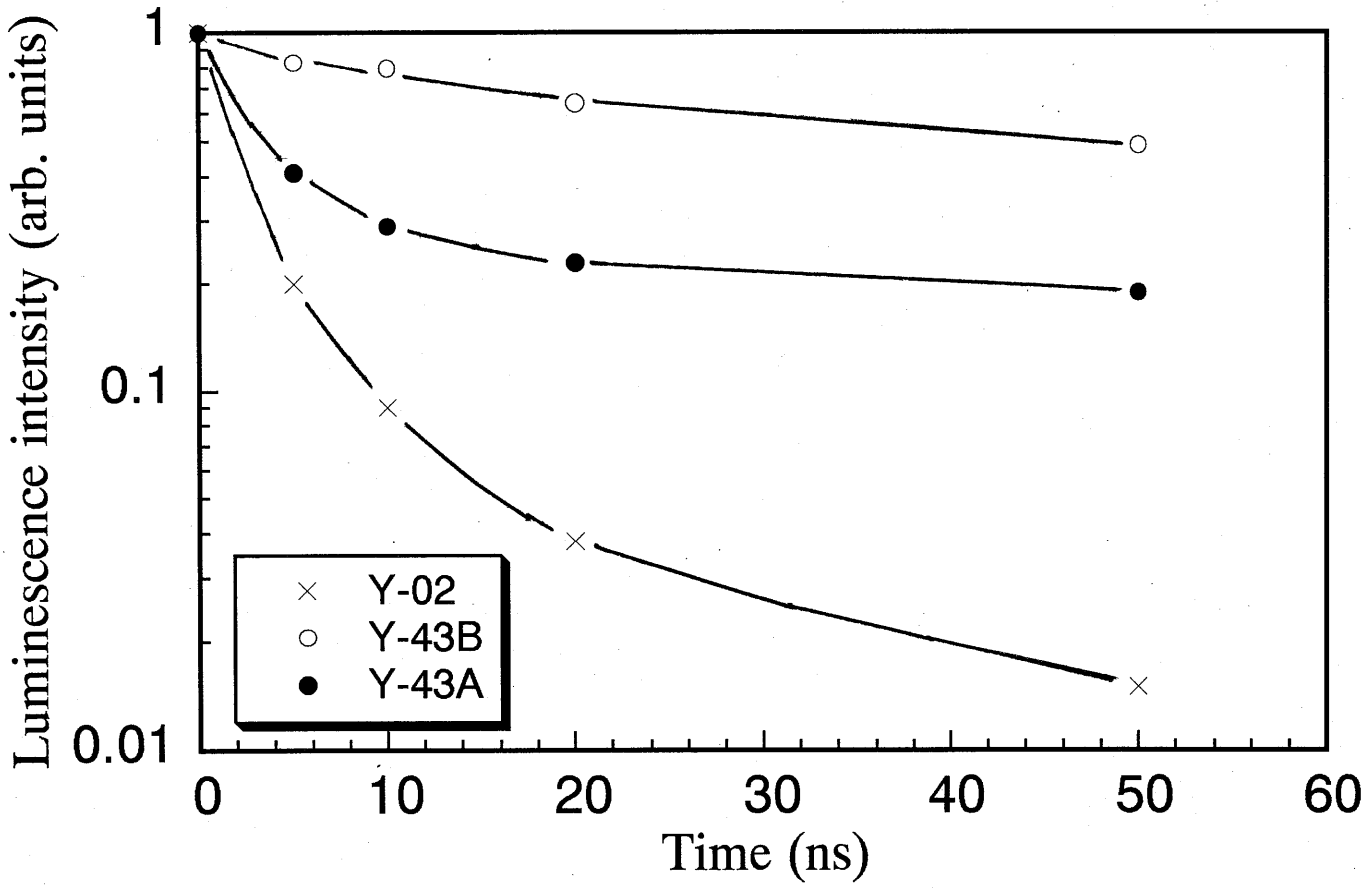
1
0.1
0.01
Luminescence intensity (arb. units)
Y-02
Y-43B
Y-43A
0
10
20
30
40
50
60
Time (ns)

Fig. 3