Japanese Journal of Applied Physics, **36** (11) (1997) 6726-6727

Laser-Induced Reversion of Photodarkening in CdS-Doped Glass

Tadaki Miyoshi, Koji Nitta, Hiroyuki Ohkuni, Fumihiko Ikeda and Naoto Matsuo

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

(Received August 4, 1997; accepted September 2, 1997)

The effect of laser irradiation on photodarkened CdS-doped glass has been investigated as a function of the wavelength of laser light, using electron spin resonance (ESR) and time-resolved luminescence. When the wavelength of laser light is tuned to 500 nm, the intensity of the ESR signal associated with photodarkening decreases, as does the decay rate of luminescence. This indicates laser-induced reversion of photodarkening.

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

Since Jain and Lind[1] first reported that semiconductor-doped glasses have a large optical nonlinearity and a fast response time, the optical properties of these materials have been investigated extensively. Roussignol *et al.*[2] reported that the response time of the nonlinear signal and the luminescence of CdS_xSe_{1-x}-doped glass decreased upon light irradiation. This photoinduced irreversible process is called photodarkening. The photodarkening is considered to be due to electrons trapped in the glass matrix[3,4] or to photoinduced defect centers which act as nonradiative recombination centers.[5,6] When photodarkened glass is heated to 400–450°C for a few hours, it recovers its original properties.[2] Here, we report the effect of laser irradiation on photodarkened CdS-doped glass, to investigate the possibility of laser-induced reversion of photodarkening.

The sample investigated was CdS-doped commercial filter glass, Toshiba Y-44, of 2.5 mm thickness. The concentration of CdS is about 0.4 wt%. The glass was 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), and then exposed to pulsed light from a tunable laser (Quanta-Ray MOPO-700; pulse duration = 5 ns, repetition rate = 11 Hz) at 300 K. 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° to the surface normal and was focused on an area of about 1 mm^2 through a quartz lens (focal length f = 150 mm). Since the peak intensity of the laser light was low (50 kW/cm^2), photoinduced spectral changes were not observed. Luminescence normal to the sample surface was collected, focused on the end of an optical fiber through two quartz lenses (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 a 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 first-derivative spectra were obtained by 100 kHz modulation. The g-values of the signals were determined using a MgO:Mn marker.

In previous papers,[7–9] we reported that defect centers are activated upon light irradiation. These activated defect centers are responsible for photodarkening. They act as nonradiative recombination centers and provide additional channels for the recombination of excited carriers; therefore the decay rate of the luminescence is increased. The ESR signal at about $g = 2.01$ is associated with the activated defect centers[9] and that at about $g = 1.99$ with the electrons trapped in the glass matrix.

We report here the effect of laser irradiation on photodarkened CdS-doped glass. Figure 1 shows the intensities of the ESR signals and luminescence of the photodarkened CdS-doped glass as a function of the wavelength of light from the tunable laser with a peak intensity of $10\,\mathrm{MW/cm^2}$. We used five samples to obtain the data points. Since these samples had already been exposed to pulsed light from the frequency-tripled Nd:YAG laser with a peak intensity of $3\,\mathrm{MW/cm^2}$, they contained activated defect centers. When the wavelength of light from the tunable laser was tuned at 500 nm, the intensities of the ESR signals decreased upon laser irradiation. The decay rate of the luminescence also decreased, and the luminescence intensity increased upon irradiation at 500 nm. These results indicate that the activated defect centers are partly passivated upon laser irradiation. Since laser light is only slightly absorbed by glass and the beam size is large (6 mm in diameter), the laser heating effect is negligibly small. Thus, passivation of the defect centers is caused by photons instead of by laser heating. In the case of thermal annealing, the ESR signal at about $g = 1.99$ disappears at 200°C and the ESR signal at about $g = 2.01$ disappears at 400°C.[9] Fig. 1

In order to investigate the origin of the wavelength dependence, we measured the ESR intensities as a function of the wavelength of laser light in CdS-doped glass before Nd:YAG laser irradiation. In this case, the defect centers are activated upon irradiation using the tunable laser. Figure 2 shows the experimental results. We used ten samples to obtain the data points. The ESR intensities are almost independent of wavelength when the wavelength of laser light is shorter than 450 nm, and the ESR signals are not observed for wavelengths longer than 500 nm. This decrease in ESR intensity is caused by a decrease in the absorbance of CdS nanocrystals. This result indicates that the photoexcited electrons and holes in CdS nanocrystals activate the defect centers. Activation occurs for light with wavelength shorter than 500 nm, since shorter-wavelength light is absorbed by CdS Fig. 2

nanocrystals. On the other hand, the wavelength dependence of passivation is different from that of activation. Passivation occurs even for longer-wavelength light. Thus, the passivation process is dominant at 500 nm, and the intensity of the ESR signal associated with photodarkening decreases upon laser irradiation at a wavelength of 500 nm. Fig. 3

Activation and passivation of the defect centers are explained using the model shown in Fig. 3. This model is an improved version of that proposed by Malhotra *et al.*[4] They considered only the process of electron trapping. On the other hand, we consider the processes of trapping and detrapping of the electrons and activation and passivation of the defect centers during laser irradiation. Figure 3 shows the processes for electrons only, for simplicity. Electrons in the valence band of CdS nanocrystals are excited to the conduction band, some of which relax to traps at the glass-semiconductor interface. Before the electrons recombine, laser light reexcites some of these trapped electrons to higher-energy surface states, from which they migrate into the glass. These electrons eventually relax to deep levels in glass. The ESR signal at about $g = 1.99$ is associated with these electrons trapped in the glass matrix. Photogenerated holes in CdS nanocrystals migrate into the interface region between CdS nanocrystals and the glass matrix, and they activate defect centers. The ESR signal at about $g = 2.01$ is associated with these activated defect centers.[9] In addition to these processes, laser light reexcites some of the trapped electrons to the conduction band of glass, and some electrons recombine with holes and passivate the defect centers. Thus, the activated defect centers are partly passivated during irradiation. The saturation of ESR intensity associated with photodarkening as a function of irradiation time[9] and the sublinear increase in ESR intensity as a function of irradiation intensity[7] are explained using this model. Details will be reported in another paper.[10]

Light with wavelength longer than 500 nm cannot generate carriers in CdS nanocrystals and does not activate the defect centers. However, this light may excite the trapped electrons in glass to the conduction band of glass, to passivate the defect centers. Thus, the intensity of the ESR signal associated with the activated defect centers, which are related to photodarkening, decreases upon laser irradiation at a wavelength of 500 nm. Malhotra *et al.*[4] reported that irradiation at 1060 nm does not reverse the darkening process. We consider that the photon energy of 1060 nm light is too low to excite the trapped electrons to the conduction band of glass.

In summary, the ESR and luminescence spectra were measured in CdS-doped glass. When photodarkened glass is exposed to laser light of long wavelength, the intensity of the ESR signal associated with the activated defect centers, which are related to photodarkening, decreases. The decay rate of luminescence also decreases. These results indicate that the activated defect centers associated with photodarkening are passivated upon laser irradiation.

This work was performed using the ESR spectrometer in the laboratory of Professor T. Miki and lasers in the Venture Business Laboratory, Yamaguchi University.

References

1) R. K. Jain and R. C. Lind: J. Opt. Soc. Am. **73** (1983) 647.
2) P. Roussignol, D. Ricard, J. Lukasik and C. Flytzanis: J. Opt. Soc. Am. B **4** (1987) 5.
3) V. Ya. Grabovskis, Ya. Ya. Dzenis, A. I. Ekimov, I. A. Kudryavtsev, M. N. Tolstoi and U. T. Rogulis: Sov. Phys. Solid State **31** (1989) 149.
4) J. Malhotra, D. J. Hagan and B. G. Potter: J. Opt. Soc. Am. B **8** (1991) 1531.
5) B. Van Wonterghem, S. M. Saltiel, T. E. Dutton and P. M. Rentzepis: J. Appl. Phys. **66** (1989) 4935.
6) M. Tomita and M. Matsuoka: J. Opt. Soc. Am. B **7** (1990) 1198.
7) T. Miyoshi, K. Towata and N. Matsuo: *Proc. Int. Conf. Optical Properties of Nanostructures, Sendai, 1994*, Jpn. J. Appl. Phys. **34** (1995) Suppl. 34-1, p. 46.
8) T. Miyoshi, K. Towata and N. Matsuo: Jpn. J. Appl. Phys. **33** (1994) 6299.
9) T. Miyoshi, K. Towata, H. Matsuki, N. Matsuo and T. Kaneda: Mater. Sci. Forum **196–201** (1995) 573.
10) T. Kaneda, T. Miyoshi, H. Furukawa, K. Nitta, H. Okuni and N. Matsuo: to be published in Nonlinear Opt.

Figure captions

Fig. 1. Intensities of ESR signals and luminescence of photodarkened CdS-doped glass, Y-44, as a function of wavelength of laser light. Luminescence intensity was measured at peak wavelength (430 nm). Curves were drawn through the data points as a guide for the eyes.

Fig. 2. Intensities of ESR signals of CdS-doped glass, Y-44, as a function of wavelength of laser light. Curves were drawn through the data points as a guide for the eyes.

Fig. 3. Model used for explaining activation and passivation of defect centers.

Fig. 1

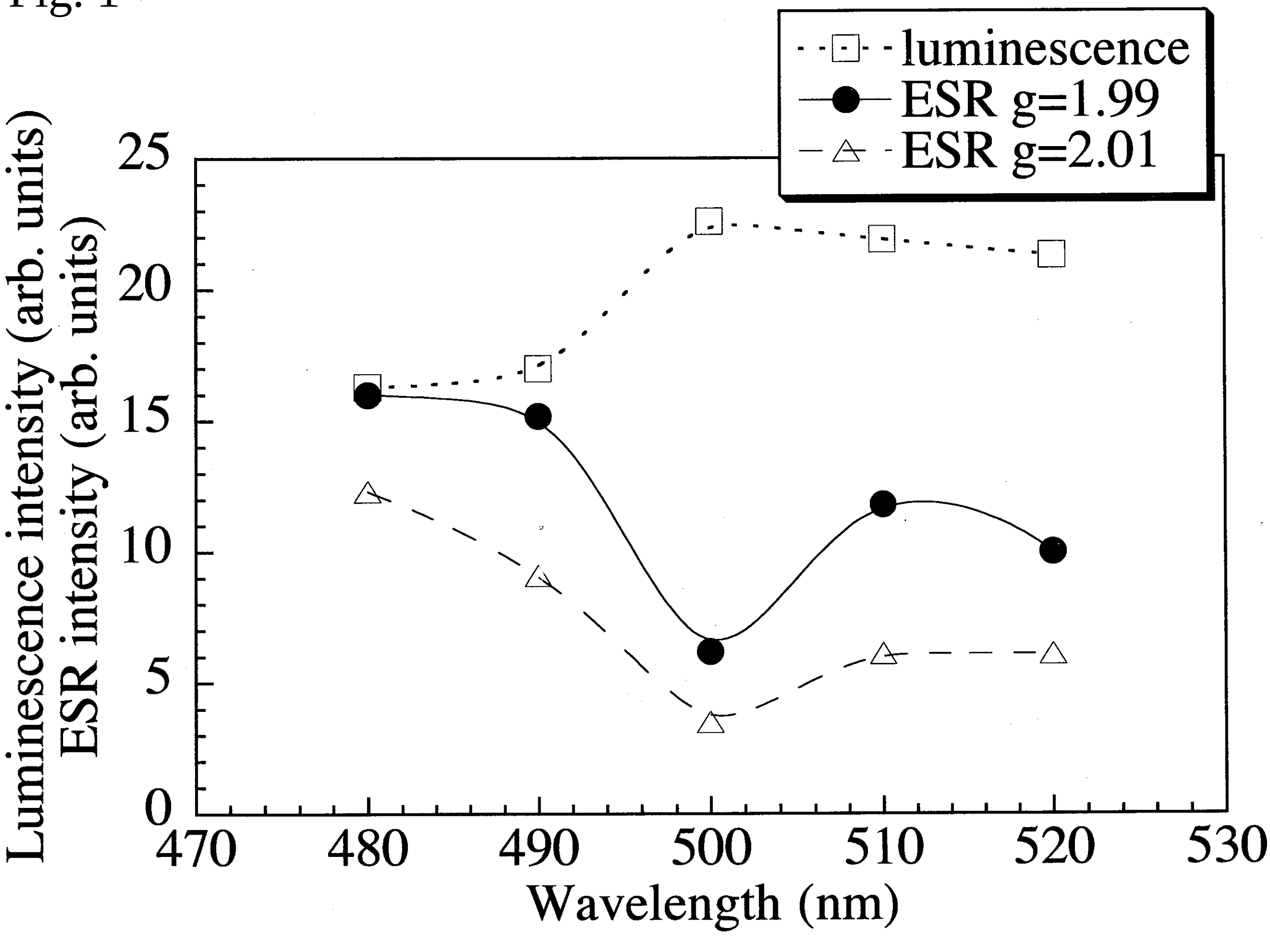

luminescence
ESR g=1.99
ESR g=2.01
Luminescence intensity (arb. units)
ESR intensity (arb. units)
0
5
10
15
20
25
470
480
490
500
510
520
530
Wavelength (nm)

Fig. 2

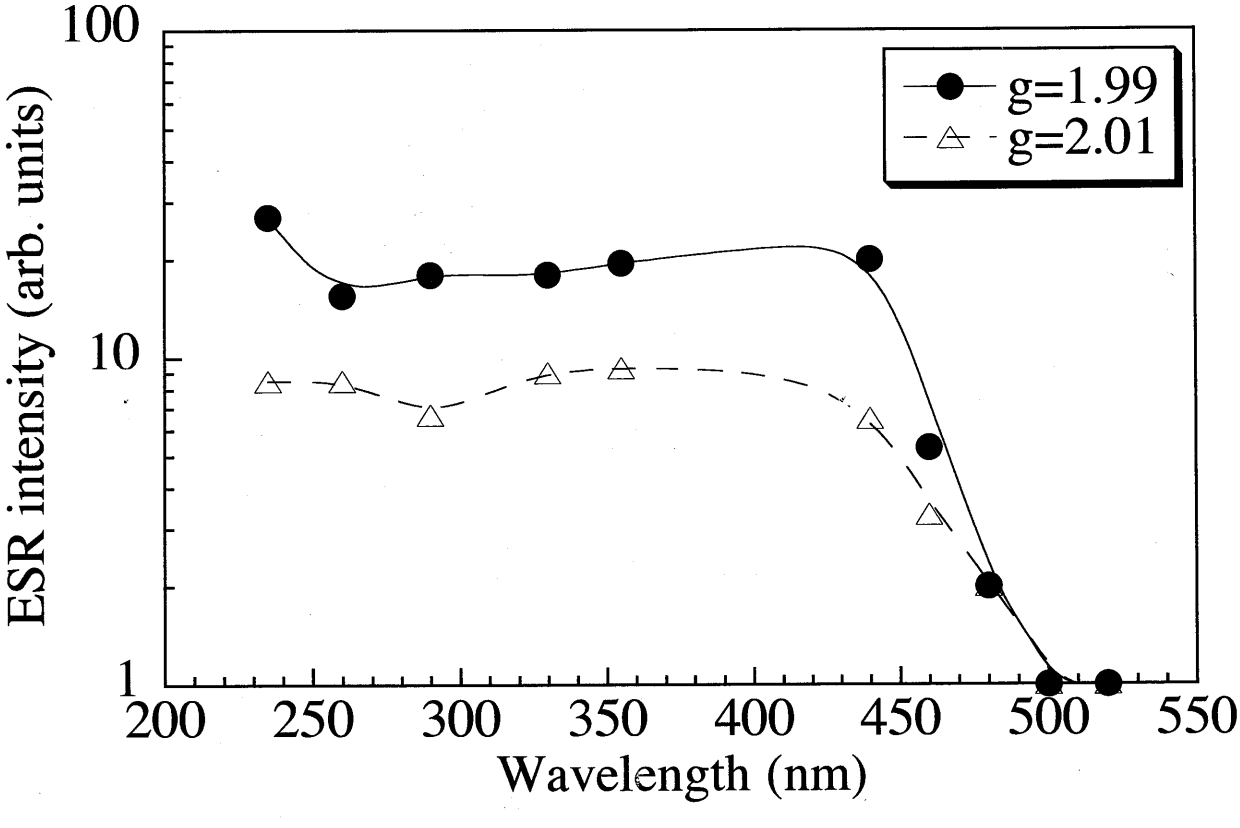
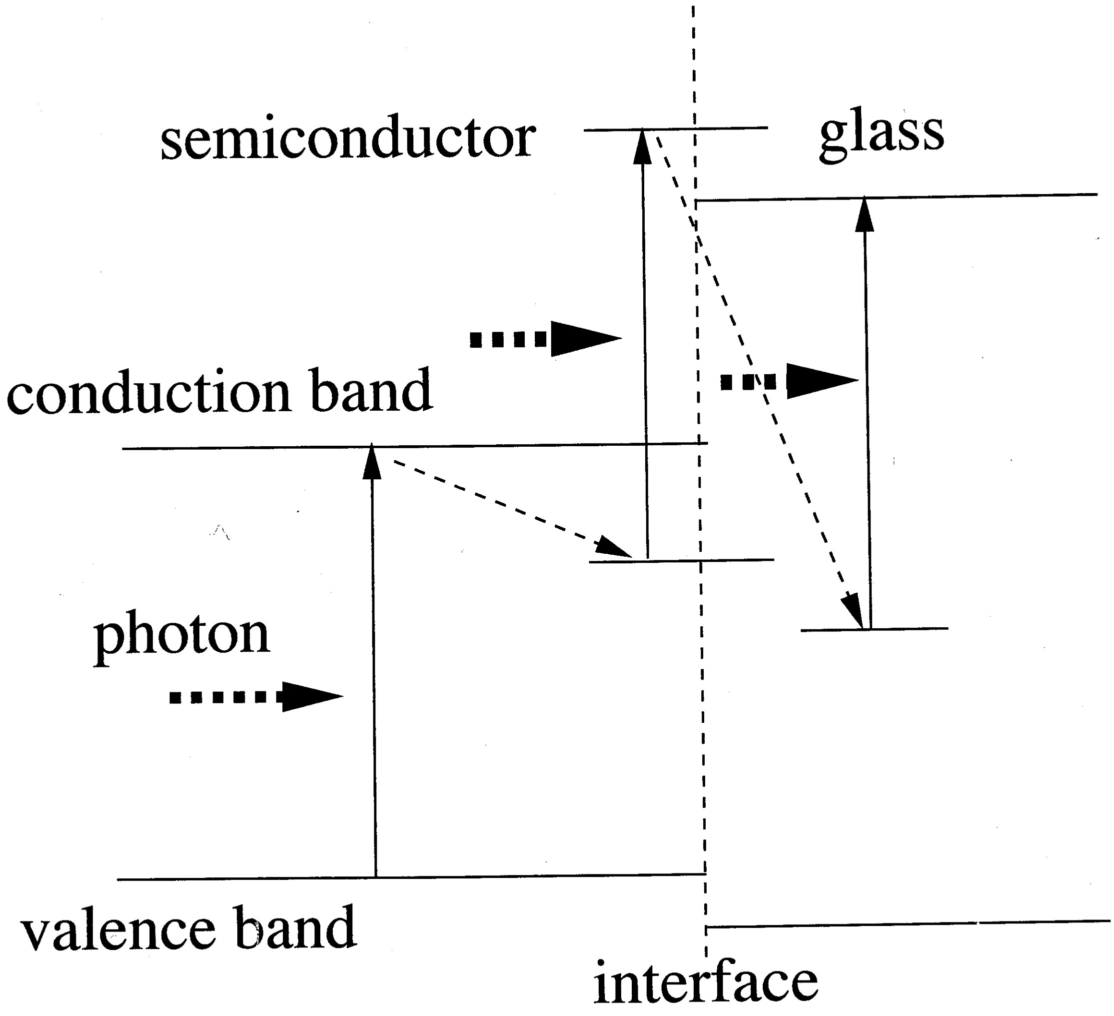

g=1.99
g=2.01
ESR intensity (arb. units)
1
10
100
200
250
300
350
400
450
500
550
Wavelength (nm)

Fig. 3



semiconductor
glass
conduction band
photon
valence band
interface