ESR of Photodarkened CdS-Doped and Undoped Glasses

Tadaki Miyoshi, Ken-ichi Towata and Naoto Matsuo

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

Electron spin resonance (ESR) and luminescence were measured in CdS-doped glass and undoped glass, which does not contain CdS microcrystals. Photoinduced centers responsible for the photodarkening effects were detected by ESR in the CdS-doped glass. This ESR signal is different from that of the host glass. This result indicates that the centers responsible for the photodarkening are not associated with the centers in the glass.

In recent years semiconductor-doped glasses have been studied extensively as nonlinear-optical materials. The optical nonlinearity and the response time are decreased by light irradiation. These photoinduced processes are called photodarkening effects. The photodarkening effects are considered to be due to traps in the host glass.[1,2] Here, we report the measurements of ESR and luminescence of CdS-doped and undoped glasses to investigate the validity of the model. We have already observed the photoinduced centers in CdSSe-doped glass after light irradiation using ESR.[3]

The samples investigated were a CdS-doped commercial glass filter (Toshiba Y-45) and host glass (Y-0) for the filter with thickness of 2.5 mm. While Y-45 contains CdS microcrystals with diameter of about 10 nm, Y-0 does not contain CdS microcrystals. The CdS-doped glass was 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. Transmittance of the glass is less than 10^{-7} at a wavelength of 337.1 nm. Thus the penetration depth of N_2 laser light is less than 0.16 mm. The host glass was exposed to pulsed light from a KrF laser (wavelength = 248 nm, pulse durations = 15 ns, peak intensity = 5 MW/cm^2, repetition rate = 10 Hz) at 300 K for 10 min. KrF laser light is absorbed at the surface region of the glass.

The ESR spectra were measured at 77 K using an X-band spectrometer (JES FE-1X). The first derivative spectra were obtained by a 100 kHz field modulation. Transient characteristics of luminescence were measured using the following apparatus at 77 K and 300 K. The excitation source was an N_2 laser (Laser Photonics LN120; wavelength = 337.1 nm, pulse duration = 300 ps, repetition rate = 7 Hz). The laser beam was set at an angle of about 30° off the normal incidence to the surface of the sample and was focused on an area about 1 mm^2 by a quartz lens (focal length f = 150 mm). The peak intensity of the laser light on the sample was about 50 kW/cm^2 (photodarkening effects were not observed at this intensity). 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 the entrance slit of a 27 cm monochromator (Jarrell-Ash Monospec 27). Time-resolved luminescence spectra were measured using an optical multi-channel analyzer with gate (Princeton Instruments D/SIDA-700). The minimum gate time is 5 ns.

Figure l (a) shows the ESR spectra of the unirradiated and light-irradiated CdS-doped glasses at 77 K. The ESR signals appear by light irradiation. The g-values of the signals are determined using a MgO:Mn marker. The ESR signals except for A and B disappear after annealing at 200 ^{o}C for 15 min, and signals A and B disappear after annealing at 400 ^{o}C for 2 h.

A luminescence peak is observed at 440 nm, which is the shallow-trap band.[4] Figure 2 shows luminescence intensities at 440 nm as a function of time at 300 K. The decay rate of the 440 nm band increases after light irradiation. Although the decay rate does not recover its initial value after annealing at 200 ^{o}C for 15 min, it recovers after annealing at 400 ^{o}C for 2 h. This correlation between the intensity of the ESR signals A and B and the response time in luminescence suggests that the centers responsible for the ESR signals A and B are associated with photodarkening effects.

Figure l (b) shows the ESR spectrum of light-irradiated host glass at 77 K. The ESR signal appears by KrF laser light irradiation and does not appear by N_2 laser light irradiation. The signal is attributable to photoinduced centers in the host glass. This signal is probably due to trapped hole centers, which have been observed in X-ray-irradiated alkali silicate glasses.[5] The g-value of the signal is different from those in the CdS-doped glass. Moreover, the diminishing temperature of the centers is about 200 ^{o}C,[5] which is lower than that for signals A and B. These results indicate that signals A and B in the CdS-doped glass are not associated with the trap centers in the glass matrix. Signals A and B may be due to the centers in the CdS microcrystals or the interface region between the CdS microcrystals and the glass matrix. We measured ESR spectra of CdS fine particles with diameter of about 100-1000 nm. However, we did not observe the effect of light irradiation on the ESR spectrum. Thus signals A and B are probably due to the centers in the interface region between CdS microcrystals and glass matrix.

Decrease in transmittance is observed in the host lass irradiated by KrF laser light. On the other hand, change in transmittance is not observed in the CdS-doped glass irradiated by N_2 laser light. This transmission change may be due to trapped electrons (or holes) in the glass matrix. Thus it is likely that a large number of electrons (holes) are trapped in the host glass and a small number of electrons (holes) are trapped in the

glass matrix of the CdS-doped glass. We consider that the traps in the glass matrix change transmittance and the photoinduced centers in the semiconductor-glass interface change response time of luminescence.

Recently, Yanagawa and Nakano[6] reported the ESR spectrum of photodarkened CdSSe-doped glass (Hoya O-54). They observed three ESR signals with g = 1.990, 1.999 and 2.010. They assigned the signals at g = 1.990 and 2.010 to electron and hole traps in the interface region, respectively. These g-values except for g = 1.990 are different from those in the present result of CdS-doped glass. The discrepancies are probably due to the difference in compositions of glass matrices and semiconductor microcrystals. A comparative study of Toshiba and Hoya glasses is in progress to elucidate the origin of the discrepancies.

In summary, ESR and luminescence of CdS-doped and undoped glasses are reported. Centers responsible for the photodarkening effects are different from those in the host glass. This result indicates that the photodarkening effects are probably due to the photoinduced centers at the glass-semiconductor interface.

References

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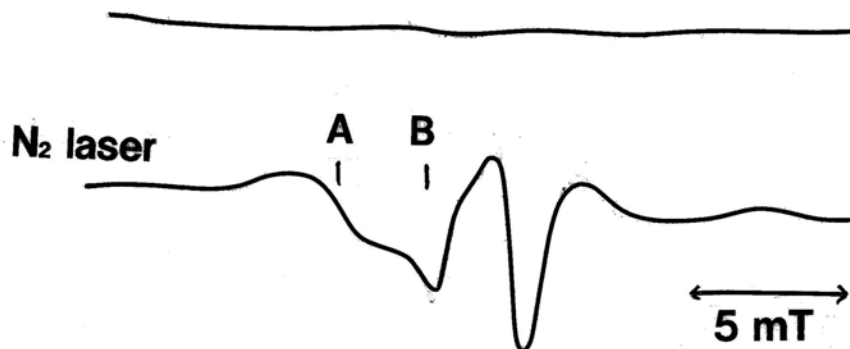
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Fig. 1. ESR spectra of glasses at 77 K: (a) CdS-doped glass (Y-45) before and after irradiation, (b) undoped glass (Y-0) after irradiation.

Fig. 2. Luminescence intensities at 440 nm of CdS-doped glass as a function of time at 300 K: before irradiation (open circles), after irradiation (solid circles) and after annealing at 400 $^{\circ}$C for 20 min (squares). Solid curves were drawn through data points as guide to the eyes. Intensities at delay time $t_d = 0$ are normalized.

Fig. 1

a) Y-45

before irrad.

N₂ laser

A   B
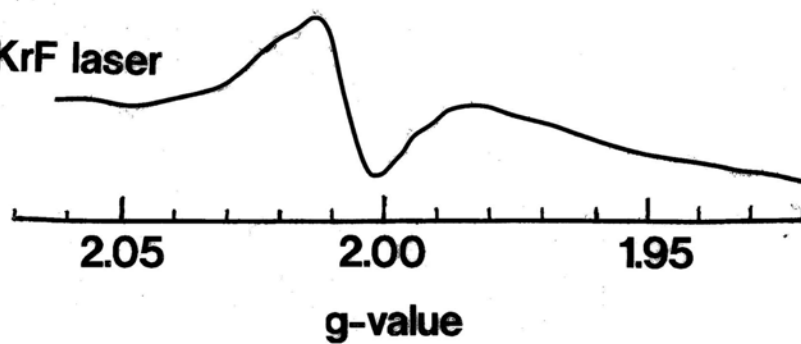
5 mT

b) Y-O

KrF laser

2.05   2.00   1.95

g-value

Fig. 2