Japanese Journal of Applied Physics, **40** (4A) (2001) 2327-2328

Thermoluminescence of Photodarkened CdS-Doped Glasses

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(Received June 22, 2000; accepted December 27, 2000)

Thermoluminescence of photodarkened CdS-doped glasses has been measured to investigate traps in glasses, which are responsible for photodarkening. Glow peaks are observed at 150–350°C in glow curves of luminescence. The location of the traps is evaluated from the glow curves.

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

Semiconductor nanocrystals in glasses (semiconductor-doped glasses) have large optical nonlinearity with a fast response time. The decay time and intensity of luminescence from CdS_xSe_{1-x}-doped glasses decrease upon light irradiation.[1)] This photoinduced irreversible process is called photodarkening. On the other hand, we observed that the intensity and decay time of luminescence from photodarkened CdS-doped glass, Toshiba Y-44, increased upon light irradiation at a wavelength of about 500 nm.[2)] This indicates that a reverse process of photodarkening (photobrightening) occurrs in CdS-doped glass upon light irradiation. Photodarkening and photobrightening are explained by the following processes.[3,4)] Electrons in the valence band of CdS nanocrystals are excited to the conduction band upon 355 nm light irradiation; they migrate into the glass, and are trapped in the glass matrix. The electrons are thought to be trapped on a Cd^{2+} ion in the glass.[5)] On the other hand, photogenerated holes in CdS nanocrystals migrate into the interface region between CdS nanocrystals and the glass matrix, and are trapped at defect centers. A possible origin of the defect is a nonbridging oxygen atom neighboring an Si atom.[5)] The centers with holes act as nonradiative recombination centers, since photogenerated electrons in semiconductor nanocrystals may recombine nonradiatively with holes trapped at the defect centers. Thus, they cause a decrease in the luminescence intensity (photodarkening). In contrast, 500 nm light cannot generate carriers in CdS nanocrystals. However, this light may excite trapped electrons to the conduction band of the glass; they migrate into CdS-nanocrystals, and some electrons recombine with holes at the defect centers. Since the centers without holes do not act as nonradiative recombination centers, the luminescence intensity increases (photobrightening).[2,6)]

Since trapped electrons in glass are considered to be excited by 500 nm light and recombine with holes in semiconductor nanocrystals, photostimulated luminescence is anticipated in photodarkened CdS-doped glasses under 500 nm light excitation. However, this is experimentally difficult to perform, since intense 500 nm light interferes with the observation of photostimulated luminescence even with the use of filters to remove the light. Thus, we measured thermoluminescence instead of photostimulated luminescence. Here, we report on the thermoluminescence of photodarkened CdS-doped glasses to investigate the traps in glasses. Photodarkening is observed when CdS-doped glasses are exposed

to intense light at room temperature, and disappears when the sample is thermally annealed at 400–450°C.[1)] These results suggest that trapping and detrapping of carriers above room temperature are related to photodarkening. Thus, we measured thermoluminescence above room temperature. Grabovskis *et al.*[7)] measured thermoluminescence in CdS-doped glass irradiated at 80 K, and they observed a glow peak at 120 K. They assigned the glow peak to thermal ionization of electron traps in the glass. Since electrons are thermally detrapped at room temperature, these traps are considered to be irrelevant to photodarkening.

The samples investigated were commercial CdS-doped filter glasses, Asahi (old name: Toshiba) L-42, Y-44, Y-46, Y-48; Hoya L-42, Y-44, Y-46, Y-48; Schott GG420, GG435, GG455, GG475; and Corning 3-74, 3-73, 3-72 and 3-71. Absorption edges of these glasses are approximately 420 nm for L-42, GG420, 3-74; 440 nm for Y-44, GG435, 3-74; 460 nm for Y-46, GG455, 3-73; and 480 nm for Y-48, GG475, and 3-71. The concentration of CdS was approximately 0.4 wt%. The 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/cm^2) for 2 min at 300 K. Thermoluminescence was measured using a TLD (thermoluminescence dosimeter) reader (Kyokko 2500). The glow curve was recorded using a pen recorder. Fig. 1

Thermoluminescence measurements were performed by heating the irradiated sample to 500°C. The heating rate was 4 K/s. The solid curve in Fig. 1 shows the glow curve of thermoluminescence for Asahi Y-44. One glow peak is observed at 210°C. From the glow curve, we evaluate the location of traps using the initial rise method.[8)] The initial rise part of a thermoluminescence curve is exponentially dependent on temperature according to

$$I = A \exp(-E/kT), \tag{0.1}$$

where A is a constant, E is the energy difference between the traps and the conduction band edge of glass and k is Boltzmann's constant. We evaluate the value of $E = 1$ eV from a plot of $ln(I)$ versus $1/T$. The evaluated value of E remains the same when the heating rate is 8 K/s, but it does change when the heating rate is 12 K/s. This indicates

that a heating rate of 4 K/s is sufficient for detailed measurement and analysis. Fig. 2

Since glass is an amorphous material, the traps are thought to be distributed in energy. A broad peak and tail on the high-temperature side indicate that this assumption is valid. The distribution of traps is confirmed by the following technique.[8] The sample is heated to a temperature T_s corresponding to a position on the low temperature tail of the glow peak. The sample is then cooled to room temperature and reheated, at the same linear rate, to 500°C. The position of the first maximum, T_m, is noted. The whole process is then repeated on a freshly irradiated sample using a new value of T_s. Fig. 2 shows the T_m–T_s curve of thermoluminescence for Asahi Y-44. A straight line with a slope of 1 indicates a quasi-continuous distribution of peaks arising from the distribution of trap depth. The value of $E = 1$ eV indicates the position of the traps nearest to the conduction band of glass.

The temperature at the glow peak is almost equal to the annealing temperature (200°C) at which the electron spin resonance (ESR) signal of trapped electrons disappears,[9] indicating that the thermal detrapping of electrons is responsible for thermoluminescence. When samples are heated, thermally excited electrons migrate into CdS nanocrystals and recombine with holes in the nanocrystals. Since some of the holes are considered to be detrapped from the defect centers, they recombine radiatively. Thus, we observe thermoluminescence. Asahi L-42, Y-46 and Y-48 show the same glow curves as Y-44.

We observed thermoluminescence in almost all of the samples investigated. The glow curves depend on the sample, and glow peaks were observed at 150–350°C. The difference in temperature of the glow peaks is thought to be due to the difference in glass composition.[10,11] Thermoluminescence is very weak in CdS-doped glasses prior to 355 nm light irradiation.

In summary, thermoluminescence was measured in CdS-doped glasses to investigate traps in the glasses. Glow peaks were observed at 150–350°C. The traps are distributed in energy. The highest trap is located about 1 eV below the conduction band of glass.

This work was performed using the laser in the Venture Business Laboratory, Yamaguchi University.

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Figure captions

Fig. 1. Glow curve of thermoluminescence for Asahi Y-44.

Fig. 2. T_{m}–T_{s} curve of thermoluminescence for Asahi Y-44.

Fig. 1

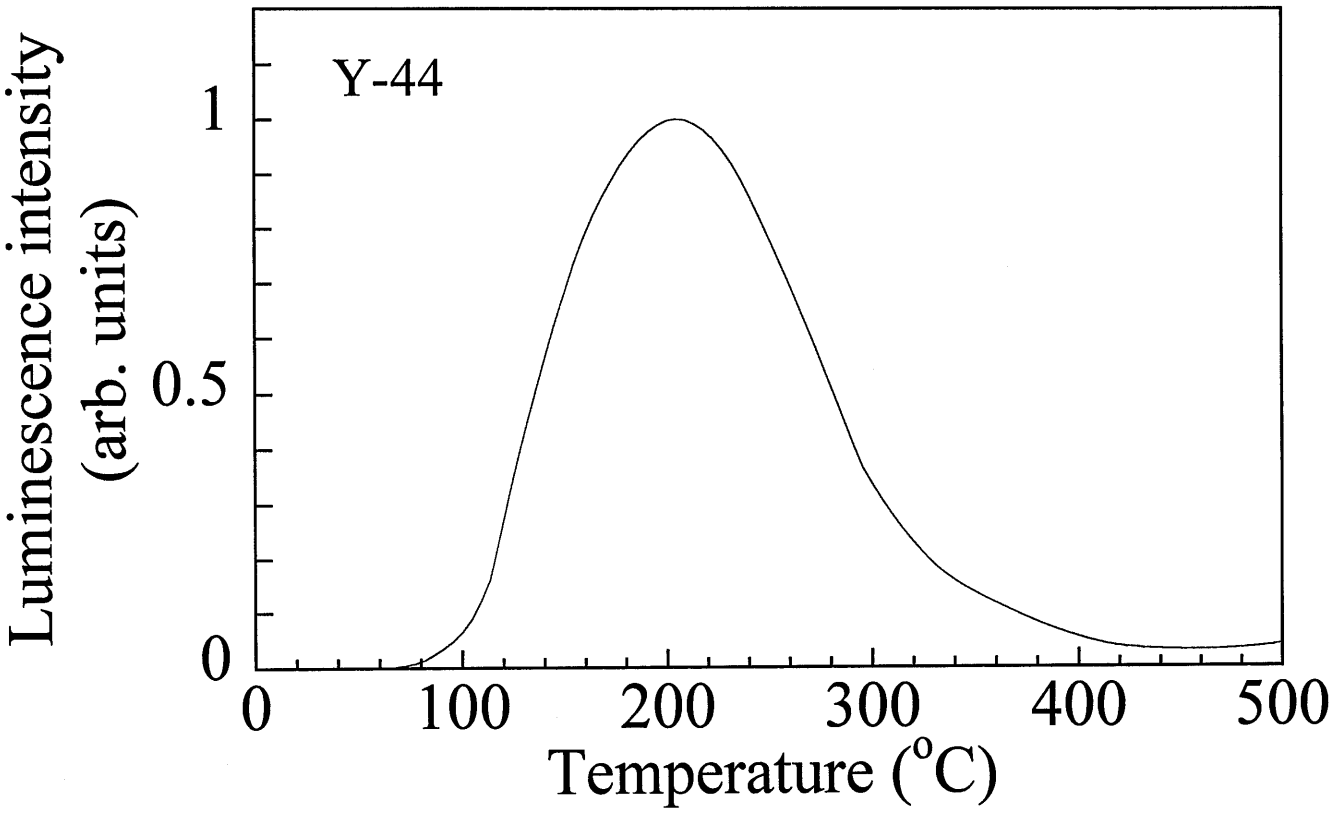
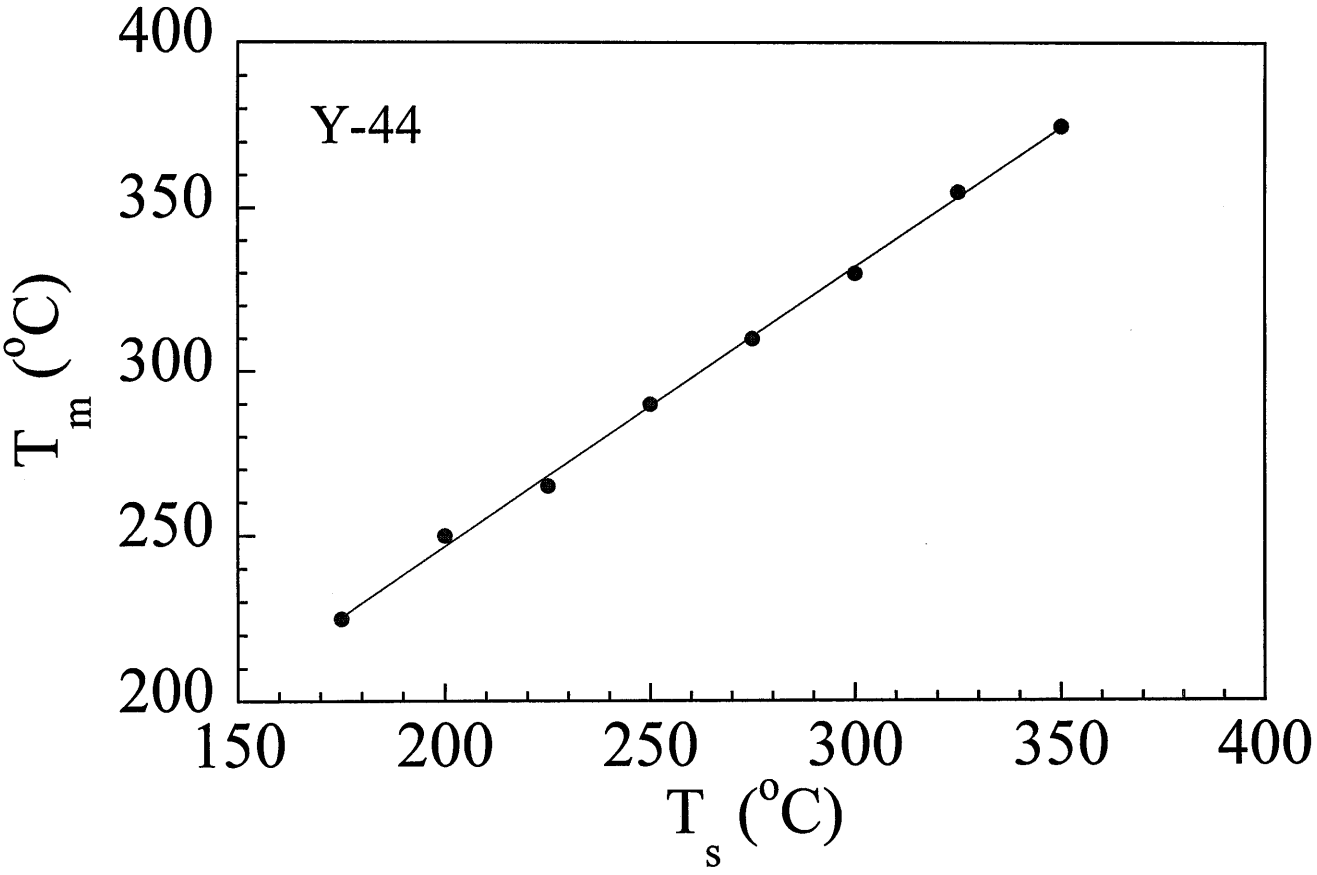

Y-44
Luminescence intensity
(arb. units)
1
0.5
0
0
100
200
300
400
500
Temperature (°C)

Fig. 2


Y-44
400
350
300
250
200
150
200
250
300
350
400
T m (°C)
T s (°C)