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Thermoluminescence of Light and X-Ray Irradiated Semiconductor-Doped Glasses

Tadaki Miyoshi, Yusuke Makidera, Takashi Kawamura, Shinya Kashima, Naoto Matsuo and Teruhisa Kaneda[1]

Department of Electrical and Electronic Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755-8611, Japan

[1]*Ube National College of Technology, Tokiwadai, Ube, Yamaguchi 755-8555, Japan*

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Thermoluminescence has been observed in light and X-ray irradiated CdS-doped glasses and light irradiated CdSSe-doped glasses. The intensity of thermoluminescence was measured as a function of irradiation intensity and irradiation time. Applicability of CdS-doped glasses as a material for a radiation dosimeter was discussed.

KEYWORDS: semiconductor, nanocrystal, X-ray irradiation, photodarkening, thermoluminescence, radiation dosimeter

Semiconductor-doped glasses have large optical nonlinearity with a fast response time.[1)] The decay time and intensity of luminescence from CdS_xSe_{1-x}-doped glasses decrease upon light irradiation.[2)] This photoinduced irreversible process is called photodarkening. Photodarkening is explained by the following process. Electrons in the valence band are excited to the conduction band upon light irradiation; they migrate into the glass, and are trapped in the glass matrix.[3)] On the other hand, photogenerated holes in semiconductor nanocrystals migrate into the interface region between semiconductor nanocrystals and the glass matrix, and are trapped at defect centers.[4)] The centers with holes act as nonradiative recombination centers.

Photodarkening disappears when the sample is thermally annealed at 400–450°C.[2)] This indicates that trapped electrons in the glass are considered to be excited by thermal energy and recombine with holes in semiconductor nanocrystals. Thus, thermoluminescence is anticipated in photodarkened semiconductor-doped glasses.[5)] In a previous paper,[6)] we reported that thermoluminescence was observed in photodarkened CdS-doped glasses. Here, we report the thermoluminescence of CdS- and CdS_xSe_{1-x}-doped glasses as a function of irradiation intensity and irradiation time. We also report the thermoluminescence of X-ray irradiated CdS-doped glass.

The samples investigated were commercial CdS-doped filter glasses, Asahi Y-44, Hoya Y-44 and Corning 3-73, and CdS_xSe_{1-x}-doped filter glasses, Asahi O-53, O-54 and O-55. Absorption edges of these glasses are approximately 440 nm for CdS-doped filter glasses, 530 nm for O-53, 540 nm for O-54 and 550 nm for O-55. The concentration of CdS and CdS_xSe_{1-x} 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) or X-ray from an X-ray diffractometer (Rigaku RV-200; Cu target, 40 kV) at 300 K. Thermoluminescence was measured using a TLD (thermoluminescence dosimeter) reader (Kyokko 2500). The glow curve was recorded using a pen recorder.

Thermoluminescence measurements were performed by heating the irradiated sample to 500°C. The heating rate was 4 K/s. One glow peak was observed at 210°C for Asahi Y-44.[6)] Figure 1 shows the intensity of thermoluminescence at the glow peak as a function of Fig. 1

irradiation intensity of laser light for Asahi Y-44. The intensity of thermoluminescence is proportional to J^2 when irradiation intensity is weak, where J is the irradiation intensity. On the other hand, the intensity of thermoluminescence is almost proportional to $J^{0.5}$ for intense irradiation.

The experimental results are explained by a two-step excitation process. Electrons in the valence band of semiconductor nanocrystals are excited to the conduction band upon light irradiation (first step excitation), some of which relax to traps at the glass-semiconductor interface. Before the electrons recombine, laser light excites some of them to higher energy surface states (second step excitation), from which they migrate into the glass. These electrons eventually relax to deep trap levels in the glass matrix.[3] Laser light reexcites some of these trapped electrons to higher energy levels in glass, some of which migrate into CdS nanocrystals and recombine with holes in the nanocrystals.[4] Since the electrons are trapped in glass via the two-step excitation process, the intensity of thermoluminescence is proportional to J^2.

The intensity dependence for intense irradiation is explained by the following rate equations.[4] The rate equation for trapped electrons in glass is

$$dN/dt = B_1 nJ - B_2 NJ, \tag{0.1}$$

where n is the number of photoexcited electrons in CdS nanocrystals, N is the number of electrons trapped in glass near CdS nanocrystals, B_1 and B_2 are rate constants. Since bimolecular recombination is dominant for intense irradiation, the value of n is proportional to $J^{0.5}$. Thus, the first term on the right-hand side becomes $B_3 J^{1.5}$, and the rate equation for N is

$$dN/dt = B_3 J^{1.5} - B_2 NJ. \tag{0.2}$$

The solution of this equation is

$$N = B_3 J^{0.5}[1 - \exp(-B_2 Jt)]/B_2. \tag{0.3}$$

When $B_2 Jt$ is larger than 1 (intense excitation and long irradiation time), the following formula is obtained approximately from eq. (0.3).

$$N = B_3 J^{0.5}/B_2. \tag{0.4}$$

The value of N is proportional to $J^{0.5}$. This is in agreement with the experimental result shown in Fig. 1 for intense irradiation intensity. This result is almost the same as that for the signal intensity of electron spin resonance (ESR).[7] Since the sensitivity of ESR is lower than the thermoluminescence, we have not observed J^2 dependence in ESR measurements. Fig. 2

Equation (0.4) predicts saturation for longer irradiation times. We measured the intensity of thermoluminescence as a function of irradiation time. Figure 2 shows the experimental results and calculated result of eq. (0.3). The intensity of thermoluminescence increases with irradiation time for a shorter irradiation time and then saturates. The calculated result (solid curve) reproduces the experimental results. Similar results were observed in all samples investigated including CdS_xSe_{1-x}-doped glasses. The values of B_3 for other samples are less than 1/10 of that for Asahi Y-44. Although the value of B_3 depends on the samples, the value of B_2 is almost independent of the samples. Fig. 3

The glow curve of thermoluminescence of the X-ray irradiated sample is the same as that of the light irradiated sample. Figure 3 shows the intensity of thermoluminescence at the glow peak as a function of current of the X-ray tube for Asahi Y-44. The intensity of thermoluminescence is proportional to the current of the X-ray tube, which is proportional to irradiation intensity. This indicates that electrons are trapped in glass via a one-step excitation process, because X-ray is high-energy radiation. Figure 4 shows the intensity Fig. 4 of thermoluminescence at the glow peak as a function of irradiation time. The intensity of thermoluminescence increases with irradiation time. The intensity dependence in X-ray irradiated CdS-doped glass is the same as those in materials for practical radiation dosimeters: LiF, BeO, $CaSO_4$, Mg_2SiO_4, and so forth. This suggests that CdS-doped glasses have potential for use as materials for radiation dosimeters. Since the temperature of the glow peak is relatively high (210°C), thermal fading may be negligible. Intensity of thermoluminescence depends on the photon energy of X-ray and gamma-rays. This energy response depends on materials, and it is considered to be modified by changing the glass composition.

In summary, thermoluminescence was measured in CdS- and CdS_xSe_{1-x}-doped glasses after light and X-ray irradiation. Dependence of thermoluminescence intensity on irradiation intensity of light and irradiation time is explained by considering the two-step excitation process and reexcitation of trapped electrons in the glass. CdS-doped glasses are possible candidates for use as materials for radiation dosimeters.

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

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Figure captions

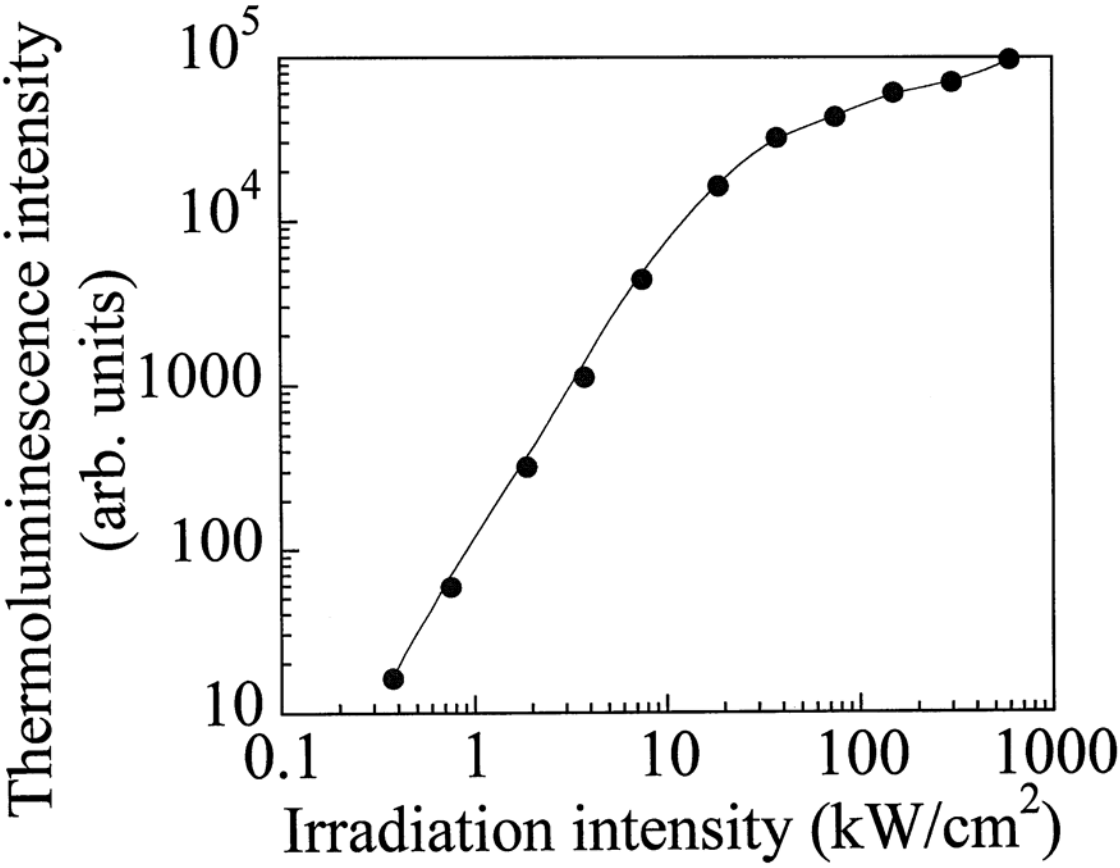
Fig. 1. Intensity of thermoluminescence as a function of irradiation intensity of laser light for Asahi Y-44. Irradiation time is 2 min. A curve was drawn through the data points as a visual guide.

Fig. 2. Intensity of thermoluminescence as a function of irradiation time of laser light for Asahi Y-44 (solid circles) and calculated result of N (solid curve). N is the number of trapped electrons in glass. The peak power density of light is 80 kW/cm^2. The parameters used for this calculation are as follows: $J = 1.4$, $B_2 = 0.01$ and $B_3 = 300$.

Fig. 3. Intensity of thermoluminescence as a function of current of the X-ray tube (irradiation intensity) for Asahi Y-44. Irradiation time is 1 min.

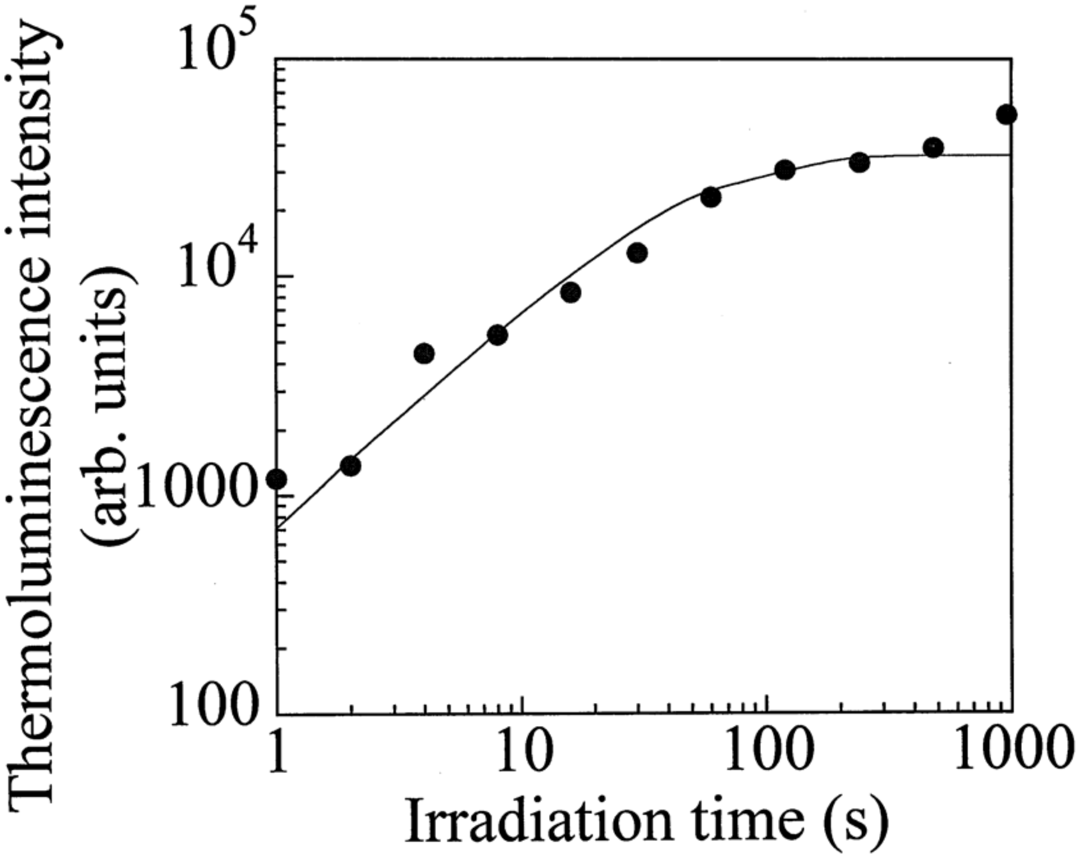
Fig. 4. Intensity of thermoluminescence as a function of irradiation time for Asahi Y-44. Current of the X-ray tube is 200 mA.

Fig. 1



Thermoluminescence intensity (arb. units)
10^5
10^4
1000
100
10
0.1
1
10
100
1000
Irradiation intensity (kW/cm^2)

Fig. 2



Thermoluminescence intensity (arb. units)
10^5
10^4
1000
100
1
10
100
1000
Irradiation time (s)

Fig. 3

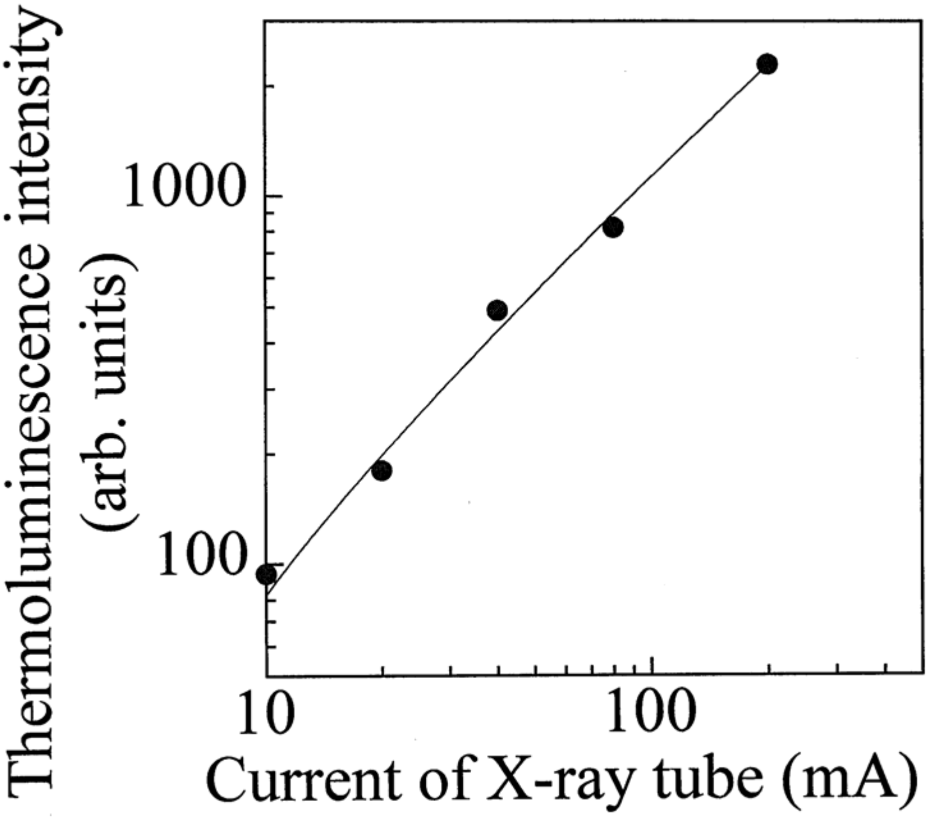
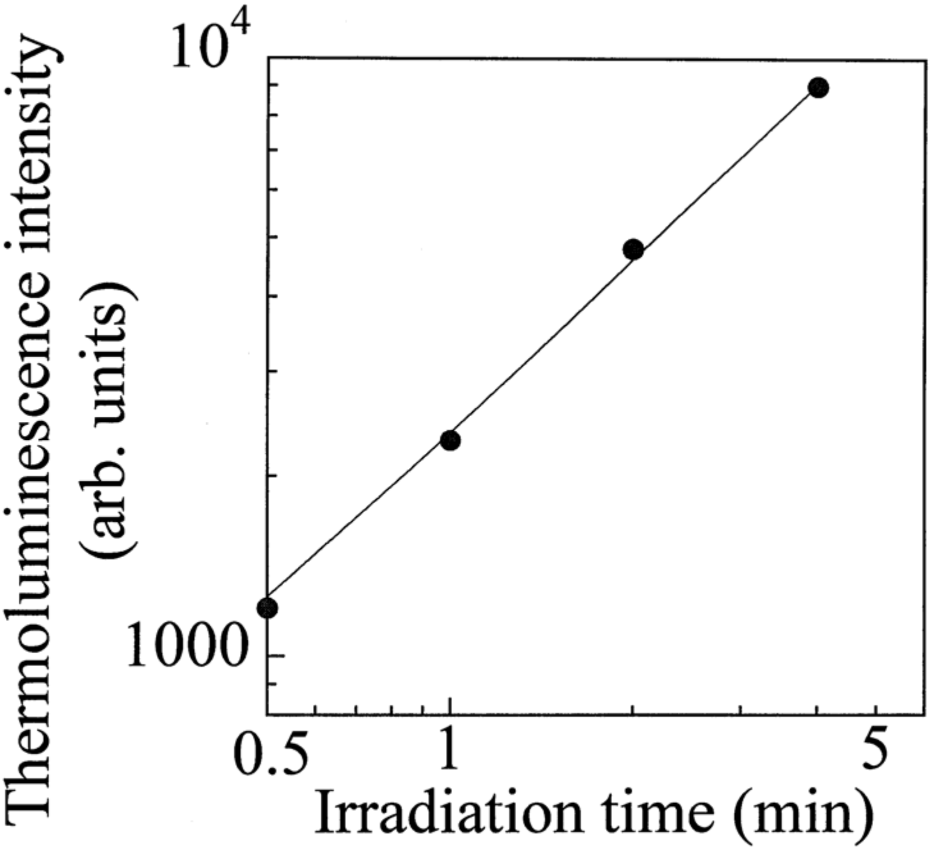

Thermoluminescence intensity
(arb. units)
1000
100
10
100
Current of X-ray tube (mA)

Fig. 4


Thermoluminescence intensity
(arb. units)
10^4
1000
0.5
1
5
Irradiation time (min)