Thermoluminescence Spectra of Laser-Irradiated CdS-Doped Glasses

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Thermoluminescence spectra have been measured in laser-irradiated CdS-doped glasses. The thermoluminescence spectra are similar to photoluminescence spectra. This indicates that the thermoluminescence is attributable to radiative recombination of electrons and holes in CdS nanocrystals.

Key Words: Semiconductor, Nanocrystal, Laser irradiation, Thermoluminescence, Photoluminescence

1. INTRODUCTION

Thermoluminescence observed is in rare-earth-doped phosphors and used for radiation dosimetry¹⁾. Grabovskis et al.²⁾ reported that thermoluminescence was observed in X-ray- and light-irradiated CdS-doped glass and thermoluminescence spectrum was identical with the photoluminescence spectrum of the CdS-doped glass. However, they showed neither glow curve of thermoluminescence above room temperature nor spectra of thermoluminescence and photoluminescence. In previous papers, we reported glow curves of thermoluminescence above room temperature in CdS-doped glasses, which were exposed to X-ray³⁾ and light⁴⁾.

Thermoluminescence in CdS-doped glasses is explained by the following process ^{5, 6).} Electrons in the valence band of CdS nanocrystals are excited to higher-energy surface states, from which they migrate into the glass. These electrons relax to deep levels in glass. Photogenerated holes remain in CdS nanocrystals. When the sample is heated, trapped electrons in the glass are considered to be excited by thermal energy and recombine radiatively with holes in CdS nanocrystals. In order to obtain information on recombination process, it is necessary to measure the spectra of the emitted thermoluminescence. Here, we report the thermoluminescence spectra of laser-irradiated CdS-doped glasses. The

thermoluminescence spectra are compared with photoluminescence spectra at high temperature.

2. EXPERIMENTAL PROCEDURE

The samples mainly investigated were commercial CdS-doped filter glasses, Asahi Y-44 and Y-46. The absorption edge of Y-44 was approximately 430 nm, and that of Y-46 was approximately 450 nm. The concentration of CdS was approximately 0.4 wt%⁷. The sizes of CdS nanocrystals were approximately 3 nm for Y-44 and 3.5 nm for Y-46⁸. Asahi Y-44 showed the most intense thermoluminescence in almost all the glasses investigated⁴.

The glasses were exposed to pulsed light from frequency-tripled Nd:YAG laser (Ekspla a PL2143B; wavelength = 355 nm, pulse duration = 30 ps, repetition rate = 10 Hz, peak power density = 240 MW/cm²) for 2 min at 300 K. The laser-irradiated sample was put on a heater. Temperature of the heater was approximately 190°C. Thermoluminescence was collected normal to the sample surface by an optical fiber, and then led to a 20 cm monochromator (Jobin Yvon CP200). Thermoluminescence spectra were measured using an optical multichannel analyzer with an image intensifier (Hamamatsu C3330). Photoluminescence spectra were measured using the same apparatus. Thermoluminescence glow curves were measured using a thermoluminescence dosimeter (TLD) reader (Kasei Optonix 2500).

3. RESULTS AND DISCUSSION

One glow peak was observed at 210°C, when the heating rate was 4 K. Figure 1 shows thermoluminescence spectrum of Y-44 at 190°C, and Fig. 2 shows photoluminescence spectrum of Y-44 at 190°C. Since excitation wavelength for photoluminescence is 355 nm, electrons and holes are generated in CdS nanocrystals. Photoluminescence band near 450 nm is attributable to the shallow trapping state-to-band type transition, and band around 550 nm is attributable to the deep-trapping state-to-band type transition in CdS nanocrystals⁹. Since thermoluminescence spectrum is similar to photoluminescence spectrum, thermoluminescence bands near 450 nm and 550 nm are considered to be attributable to the same type of transitions. Therefore. thermoluminescence is attributable to radiative recombination of electrons and holes in CdS nanocrystals. When the sample is heated, electrons are provided from traps in glass, and holes from the defect centers in the interface region.



Figure 1 Thermoluminescence spectrum of laser-irradiated CdS-doped glass, Asahi Y-44.

Figure 3 shows thermoluminescence spectrum of Hoya Y-48. This sample is also CdS-doped filter glass. However, the intensity of thermoluminescence in Hoya Y-48 is 1/50 of that in Asahi Y-44. A broad band around 800 observed nm is in thermoluminescence spectrum. This band is approximately represented by a Gaussian curve (solid curve) with peak wavelength of 770 nm and full width at half maximum (FWHM) of 380 nm. Similar spectra were observed in almost all samples, which show weak thermoluminescence. Therefore, the band may not be originated from CdS nanocrystals. Possible origin of the band is localized levels in glass matrix. Since the band decreases during heating, it is not due to thermal radiation.



Figure 2 Photoluminescence spectrum of CdS-doped glass, Asahi Y-44, under laser excitation at 190° C.



Figure 3 Thermoluminescence spectrum of laser-irradiated CdS-doped glass, Hoya Y-48. Solid curve is a Gaussian curve with peak wavelength of 770 nm and full width at half maximum (FWHM) of 380 nm.

Figure 4 shows thermoluminescence spectrum of Asahi Y-46. Solid circles show measured spectrum, sold curve is the Gaussian curve with peak wavelength of 770 nm and FWHM of 380 nm, and solid triangles show subtracted spectrum, which is the difference between the measured spectrum and the Gaussian curve. The subtracted spectrum is similar to photoluminescence spectrum shown in Fig. 5. Luminescence band shifts to longer wavelength side in comparison with that of Y-44. This is due to difference in band gap energy, E_g . The value of E_g of CdS in Y-46 is smaller than that in Y-44. This confirms that the luminescence band is originated from CdS nanocrystals.



Figure 4 Thermoluminescence spectrum of laser-irradiated CdS-doped glass, Asahi Y-46. Solid circles show measured spectrum, solid curve is the Gaussian curve with peak wavelength of 770 nm and FWHM of 380 nm, and solid triangles show subtracted spectrum, which is the difference between the measured spectrum and the Gaussian curve.



Figure 5 Photoluminescence spectrum of CdS-doped glass, Asahi Y-46, under laser excitation at 190 °C.

4. CONCLUSION

Thermoluminescence spectra have been measured in laser-irradiated CdS-doped glasses. The spectra are compared with photoluminescence spectra. The thermoluminescence spectra are similar to the photoluminescence spectra. Thermoluminescence bands are attributable to the shallow trapping state-to-band type transition, and to the deep-trapping state-to-band type transition in CdS nanocrystals.

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(Received August 31, 2007)