J Mater Sci (2008) 43:1013–1015
DOI 10.1007/s10853-007-2243-0

Induced absorption in X-ray-irradiated CdS- and CdSSe-doped glasses

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Received: 6 July 2007 / Accepted: 19 October 2007 / Published online: 15 November 2007

Abstract Optical transmission spectra of X-ray-irradiated CdS- and CdSSe-doped glasses and undoped glass have been measured. Induced absorption has been observed in these glasses. In addition to the radiation-induced absorption increment, decrease in absorption has been observed near absorption edge in CdSSe-doped glasses. Origin of the decrease in absorption was examined.

Introduction

X-ray irradiation effects in semiconductor-doped glasses have been reported. Grabovskis et al. [1] reported that the induced absorption was observed in the X-ray-irradiated CdS-doped glasses. On the other hand, Gomonnai et al. [2] reported decrease in absorption near absorption edge in CdSSe-doped glass. In a previous article, we reported optical transmission spectra of X-ray irradiated CdS-doped glass [3]. We observed increase in absorption. This is different from that reported by Gomonnai et al. [2]. Here, we report optical transmission spectra of X-ray irradiated CdS-doped glasses, CdSSe-doped glasses, and undoped glass in order to examine the origin of the difference.

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Experimental procedure

The samples investigated were commercial CdS-doped filter glasses, Asahi L-42, Y-44 and Y-46, and CdSSe-doped filter glasses, Asahi O-56 and R-60. Host glass (Y-0) for the filters was also investigated for comparison. Y-0 does not contain semiconductor nanocrystals. The glass composition was 70% SiO_2, 10% Na_2O, 10% ZnO, 6% K_2O, and 3% B_2O_3 [4]. Absorption edges of the glasses were approximately 410 nm for L-42, 430 nm for Y-44, 450 nm for Y-46, 550 nm for O-56, and 590 nm for R-60. The size of the sample was 10 mm in width and length and 2.5 mm in thickness. The concentration of CdS and CdSSe was approximately 0.4 wt% [4]. Alloy composition was determined by Raman scattering [5]: $CdS_{0.23}Se_{0.77}$ for O-56 and $CdS_{0.12}Se_{0.88}$ for R-60.

The glass was exposed to X-rays from an X-ray source (Hitachi Medico MBR-1520R, W target, 150 kV, 20 mA) at 300 K. Low energy X-rays were eliminated using a filter, which was composed of an Al plate and a Cu plate. The effective X-ray energy was 48 keV using both an Al plate with a thickness of 0.5 mm and a Cu plate with a thickness of 0.1 mm. The X-ray dose was 20 Gy. Transmission spectra were measured using a spectrophotometer (JASCO V-550) at 300 K.

Results and discussion

Figure 1 shows transmission spectra of X-ray-irradiated and unirradiated CdS-doped glass, Y-44, and undoped

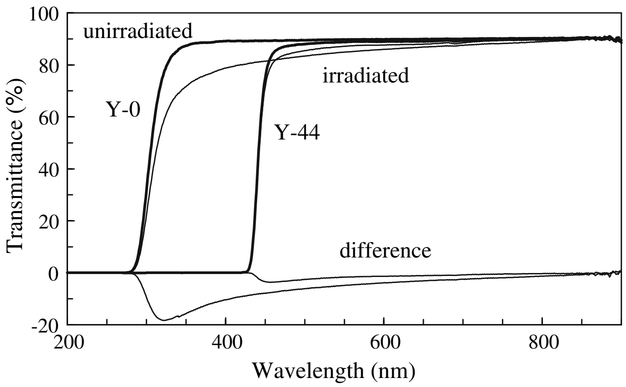

Fig. 1 Transmission spectra of X-ray-irradiated and unirradiated CdS-doped glass, Y-44, and undoped glass, Y-0, at 300 K. Thick curves indicate spectra for unirradiated samples and thin curves for irradiated samples. Differential transmission spectra are also shown. The X-ray dose is 20 Gy and the effective X-ray energy is 48 keV

glass, Y-0, at 300 K. Differential transmission spectra are also shown. Differential transmittance is negative. This indicates that radiation-induced absorption increment (decrease in transmittance) is observed in the irradiated glasses. The induced absorption of Y-0 is larger than that of Y-44. The induced absorption is observed in all CdS-doped glasses investigated.

Figure 2 shows transmission spectra of X-ray-irradiated and unirradiated CdSSe-doped glass, O-54, at 300 K. Differential transmission spectrum is also shown. Differential transmittance is negative for wavelengths longer than about 560 nm, and it is positive around 555 nm. This indicates that decrease in absorption (increase in transmittance) is observed near absorption edge in CdSSe-doped glass in addition to the induced absorption (decrease in transmittance). The decrease in absorption is also observed in other CdSSe-doped glasses investigated.

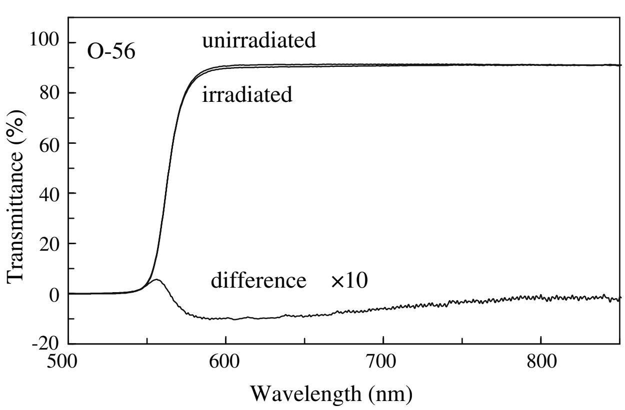

Fig. 2 Transmission spectra of X-ray-irradiated and unirradiated CdSSe-doped glass, O-54, and differential transmission spectrum, at 300 K. The X-ray dose is 20 Gy and the effective X-ray energy is 48 keV

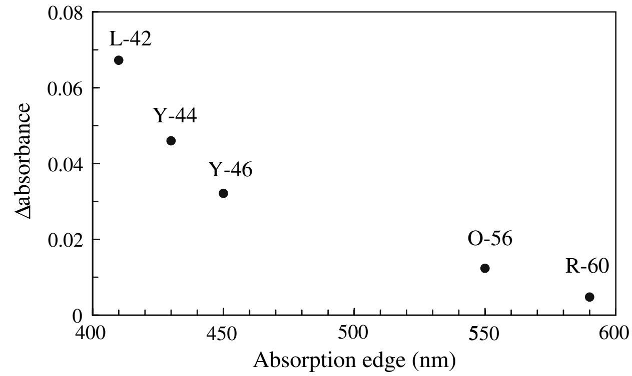

Fig. 3 Induced absorption of CdS- and CdSSe-doped glasses as function of absorption edges of the samples. The X-ray dose is 20 Gy and the effective X-ray energy is 48 keV

Figure 3 shows the induced absorption as function of absorption edges of the samples. The induced absorption is the peak value in the differential transmission spectrum of each sample. The induced absorption decreases with increasing wavelength of absorption edge. The induced absorption of Y-0 is 0.16, which is larger than those of CdS- and CdSSe-doped glasses. This suggests that the induced absorption is attributable to glass matrix.

Gomonnai et al. [2, 6] reported the radiation-induced absorption increment in alkali borosilicate glass matrix exposed to X-ray and electron irradiation. The additional absorption bands are attributed to intrinsic hole radiation color centers H_3^+, H_2^+, and H_4^+ [6]. The bands corresponding to H_3^+ and H_2^+ centers vanish with thermal annealing at 200 °C. On the contrary, the induced absorption shown in Fig. 1 does not vanish with annealing at 200 °C [3]. Therefore, the induced absorption in Fig. 1 is considered to be attributable to lower energy tail of the absorption band corresponding to H_4^+ centers.

The decrease in absorption is observed in $CdS_{0.23}Se_{0.77}$-doped glass, O-56 (Fig. 2), and in $CdS_{0.12}Se_{0.88}$-doped glass, R-60. Gomonnai et al. [2] reported the decrease in absorption near absorption edge in $CdS_{0.4}Se_{0.6}$-doped glass. They observed blue shift of absorption edge in irradiated samples, which causes the decrease in absorption near absorption edge. They considered that the blue shift of the absorption edge was attributable to X-ray ionization of CdSSe nanocrystals with charge carrier transfer between the nanocrystals and the glass matrix, as well as to the additional hydrostatic pressure upon nanocrystals due to the radiation-induced swelling of the glass matrix [2]. On the other hand, they observed increase in absorption in undoped glass. This result is consistent with the present result of Y-0 shown in Fig. 1. In undoped glass and CdS-doped glasses, the increase in absorption is large as shown in Figs. 1 and 3. Consequently, the increase in absorption is observed in CdS-doped glasses, and the decrease in absorption is not observed in these glasses. Since the increase in absorption is small in CdSSe-doped glasses as shown in Figs. 2 and 3, the decrease in absorption is observed in CdSSe-doped glasses.

Conclusion

Induced absorption has been observed in X-ray-irradiated CdS-doped and undoped glasses. In addition to the induced absorption, decrease in absorption has been observed in CdSSe-doped glasses. The induced absorption is attributable to intrinsic hole radiation color centers, and the decrease in absorption to X-ray ionization of CdSSe nanocrystals or radiation-induced swelling of the glass matrix.

Acknowledgement This work was performed using the spectrophotometer in the laboratory of Professor K. Kasatani. The authors are grateful to Professor K. Kasatani.

References

1. Grabovskis VY, Dzenis YY, Ekimov AI, Kudryavtsev IA, Tolstoi MN, Rogulis UT (1989) Sov Phys Solid State 31:149
2. Gomonnai AV, Azhniuk YM, Kranjcec M, Solomon AM, Lopushansky VV, Megela IG (2001) Solid State Commun 119:447
3. Miyoshi T, Ushigusa K, Tamechika M, Tokuda N, Kaneda T (2007) Jpn J Appl Phys 46:5313
4. Yanagawa T, Nakano H, Ishida Y, Kubodera K (1993) Opt Commun 100:118
5. Miyoshi T, Nakatsuka T, Matsuo N (1995) Jpn J Appl Phys 34:1835
6. Gomonnai AV, Azhniuk YM, Goyer DB, Megela IG, Lopushansky VV (2001) J Optoelectr Adv Mater 3:37