Journal of Optoelectronics and Advanced Materials, Vol. 3, No. 2, June 2001, p. 509 - 514

X-RAY EXCITED LUMINESCENCE AND X-RAY IRRADIATION EFFECT ON $CdS_{1-x}Se_x$ NANOCRYSTALS OPTICAL ABSORPTION

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X-ray excited luminescence and X-ray irradiation (10–3240 Gy) effect on the optical absorption spectra of $CdS_{1-x}Se_x$ nanocrystals in borosilicate matrix are studied. The parameters of the luminescence bands are analyzed with the account of the luminescence of the host matrix itself. The observed smearing of quantum-size-related maxima and absorption edge blue shift with the irradiation dose increase are related to the X-ray ionization of the nanocrystals with charge-carrier transfer between the nanocrystals and the host matrix. The radiation-induced changes completely vanish at post-irradiation annealing to 575 K.

(Received June 1, 2001; accepted June 11, 2001)

Keywords: Nanocrystals, Semiconductors, Luminescence, X-ray irradiation, Optical absorption

1. Introduction

$CdS_{1-x}Se_x$ nanocrystals (quantum dots) embedded in glass matrices are extensively studied in the recent years by optical techniques, providing important information on the nanocrystal parameters. Optical absorption, Raman scattering and photoluminescence (PL) enable one to derive the nanocrystal composition, size and energy parameters, complementing the methods of electron microscopic studies, small-angle X-ray scattering and Auger spectroscopy [1–5]. PL spectra are known to be essentially dependent on the excitation energy and power [1, 6–8], hence it seems interesting to investigate X-ray excited luminescence (XL) as well. The luminescent properties of the glass matrix itself should be also taken into account at the analysis of the observed spectra of the glass-embedded nanocrystals.

Only a few studies devoted to the variation of quantum dot parameters under irradiation with X-rays [9, 10] and high-energy electrons [11] are reported. It should be noted that X-ray irradiation effects have been discussed only for CdS quantum dots in the interband absorption range, no detailed dose dependences being shown, especially for the spectral range where specific quantum-size effects in the absorption spectra are revealed.

Here we report the results of XL spectroscopic studies as well as the influence of X-ray irradiation upon the optical absorption spectra of $CdS_{1-x}Se_x$ nanocrystals embedded in borosilicate glass matrix.

2. Experimental

$CdS_{1-x}Se_x$ quantum dots were embedded in a matrix of SiO_2–B_2O_3–ZnO–K_2O–Na_2O glass by conventional solid-state precipitation technique generally similar to those described in [3, 12, 13]. About 5×5 mm^2 plates with the thickness down to 0.13 mm were prepared for optical measurements.

X-ray irradiation and X-ray luminescence excitation was provided by a molybdenum anticathode tube (40 kV, 20 mA) with the irradiation dose rate of 0.15 Gy/s what enabled us to achieve the irradiation dose *D* up to 3240 Gy, its value was determined by LiF thermoluminescent gauges. The interval between the irradiation and the beginning of the measurement procedure was 1 h. Optical absorption measurements were performed at room temperature on a LOMO MDR-23 monochromator with FEU-100 and FEU-62 phototubes in the range 300–800 nm.

3. Results and discussion

XL spectra of $CdS_{1-x}Se_x$ nanocrystals in the glass matrix are shown in Fig. 1. The XL of the borosilicate glass matrix itself, measured separately, is presented by the dashed curve. The band, centered at 470 nm (2.64 eV) is related to intrinsic and radiation-induced centres in glass. Note that a similar luminescence band is observed in glassy SiO_2 under X-ray excitation [14] and in alkali borosilicate glasses under N_2-laser excitation [15]. Having subtracted the host matrix contribution from the experimentally measured spectra of the glass-embedded nanocrystals, we obtained the spectra, shown by solid curves, whose simulation by elementary Gaussian contours (dotted curves) provided the energy position and halfwidth values of $CdS_{1-x}Se_x$ nanocrystal XL bands. Thus, in the XL spectra the bands centered at 2.04 and 2.36 eV with the halfwidths 0.35 and 0.54 eV, respectively (for $CdS_{0.4}Se_{0.6}$), and at 1.92 and 2.21 eV with the halfwidths 0.30 and 0.38 eV, respectively (for $CdS_{0.22}Se_{0.78}$), have been detected.

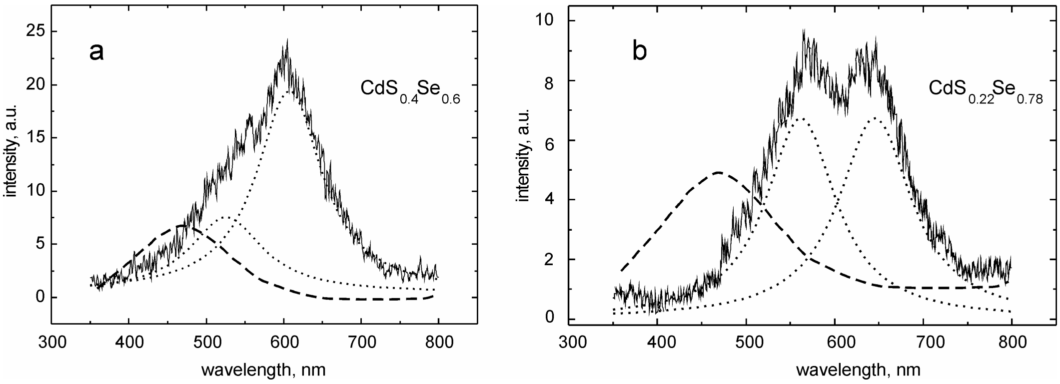

Fig. 1. X-ray excited luminescence spectra of $CdS_{0.4}Se_{0.6}$ (a) and $CdS_{0.22}Se_{0.78}$ (b) nanocrystals embedded in alkali zinc borosilicate glass matrix: dashed curves – XL of the host matrix itself; solid curves – the experimentally measured spectra of the samples after subtraction of the matrix luminescence; dotted curves – simulation of the nanocrystals spectra by Gaussian contours.

It should be noted that the composition of $CdS_{1-x}Se_x$ nanocrystals in the glass matrix was determined from the measured Raman scattering spectra (room temperature, 488.0-nm laser excitation, LOMO DFS-24 double grating monochromator). Since $CdS_{1-x}Se_x$ mixed crystals are characterized by the two-mode type of phonon spectrum compositional transformation, having compared the observed CdS-related (285 and 275 cm^{-1}) and CdSe-related (200 and 208 cm^{-1}) LO phonon frequencies with the known results for $CdS_{1-x}Se_x$ nanocrystals in a broad compositional range [16–18], we obtained for the samples under investigation the values of x=0.6 and 0.78, respectively.

The effect of X-ray irradiation on the optical absorption spectra of $CdS_{1-x}Se_x$ nanocrystals in borosilicate glass matrix is shown in Fig. 2. The additional singularities revealed in the non-irradiated samples spectra (solid curves in Fig. 2, a, b) are known to arise due to charge-carrier confinement in case the semiconductor nanocrystal characteristic size not exceeding the exciton Bohr radius [1]. This has enabled us to derive, based on [5], from the experimentally observed spectra the average radius r = 2.76 nm and 3.08 nm for $CdS_{0.4}Se_{0.6}$ and $CdS_{0.22}Se_{0.78}$ nanocrystals, respectively.

In $CdS_{0.4}Se_{0.6}$ nanocrystals the confinement-related absorption maxima are observed at X-ray irradiation with the dose *D* up to 135 Gy (Fig. 2, a). With the further increase of the irradiation dose they smear and vanish. At $D \geq 540$ Gy the absorption edge is smooth and gradually shifts towards higher energies with the irradiation dose increase (See Fig. 2, a).

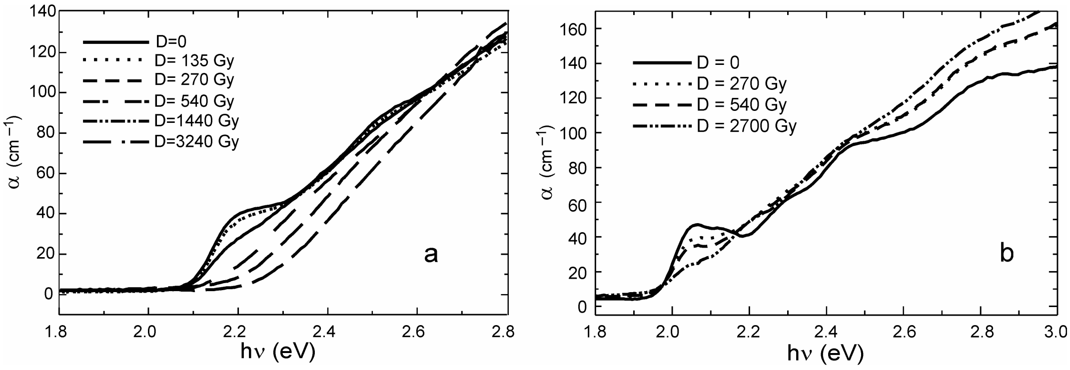

Fig. 2. X-ray irradiation effect on the optical absorption spectra of $CdS_{0.4}Se_{0.6}$ (a) and $CdS_{0.22}Se_{0.78}$ (b) nanocrystals embedded in alkali zinc borosilicate glass matrix.

As seen from Fig. 2, b, in $CdS_{0.22}Se_{0.78}$ nanocrystals the X-ray irradiation effect is also revealed in the quantum-size absorption maxima smearing. However, this applies mostly for the first (lowest-energy) and second maxima, though these two features do not vanish completely even at the highest achieved irradiation dose values (2700 Gy). Besides, the second maximum, whose energy position (2.28 eV) remains unchanged at D≤270 Gy, smears almost completely with the further increase of the irradiation dose, and at D≥1080 Gy arises again at 2.20 eV. The energy of the first quantum-size maximum also shifts downward, though much less. Meanwhile, the higher-order features in the absorption spectrum remain unchanged even at 2700 Gy. The dependence of the energy positions of the quantum-size maxima on the X-ray irradiation dose is illustrated by Fig. 3.

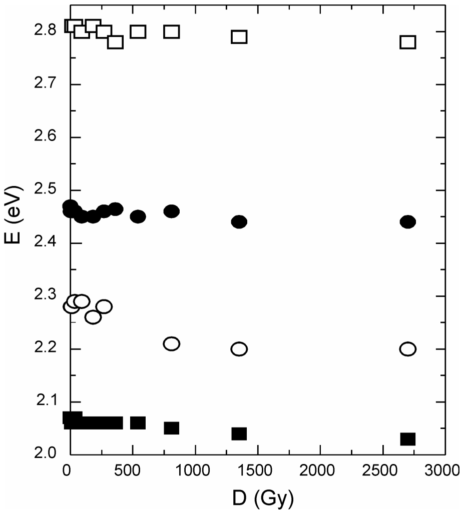

Fig. 3. Dependence of the energy positions of the confinement - related maxima in the optical absorption spectra of $CdS_{0.22}Se_{0.78}$ nanocrystals on the X-ray irradiation dose.

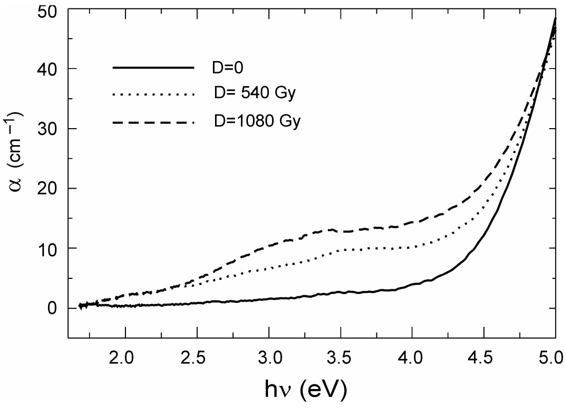

Fig. 4. X-ray irradiation effect on the optical absorption spectra of alkali zinc borosilicate glass matrix.

The effect of X-ray irradiation on the absorption spectra of alkali zinc borosilicate glass matrix itself is shown in Fig. 4. The broad irradiation-induced absorption increment can be simulated by a superimposement of three Gaussian contours centered at 1.75, 3.04 and 4.29 eV. Such bands are known to appear in silicate glasses under UV, X-ray, γ- and electron irradiation and are attributed to colour centres in glass [19–21].

It should be noted that in X-ray irradiated $CdS_{1-x}Se_x$ quantum dots in the borosilicate glass matrix the irradiation-induced blue shift of the absorption edge whas observed to decrease slightly after storage at room temperature. In particular, as seen from Fig. 5, for the most heavily irradiated (3240

Gy) $CdS_{0.4}Se_{0.6}$ sample the absorption edge position shifts by 0.045 eV after six-day (150 h) storage, the major part of this value arising from the first 24 h. Note that further storage during 1000 h results in no changes in the absorption spectrum. Such effect can be attributed to the post-irradiational relaxation which is generally typical for dielectric glass matices [22].

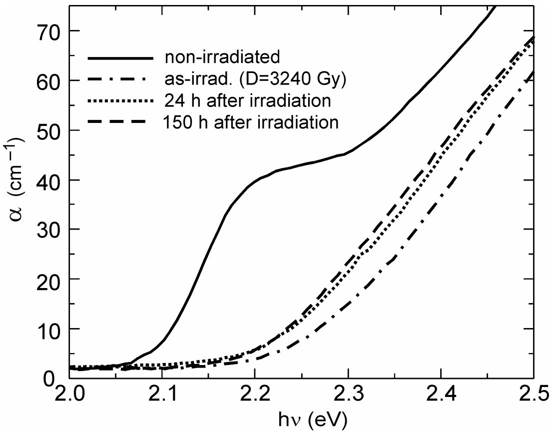

Fig. 5. Post-irradiation storage effect on the optical absorption spectrum of 3240-Gy X-ray irradiated $CdS_{0.4}Se_{0.6}$ nanocrystals embedded in alkali zinc borosilicate glass matrix.

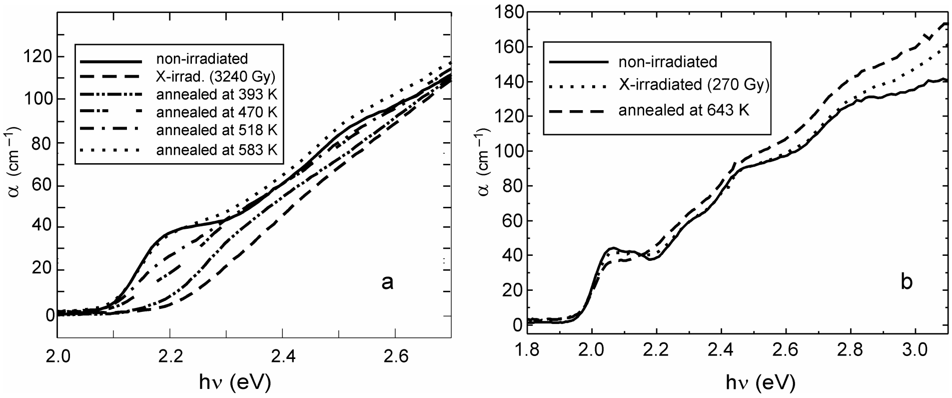

Fig. 6. Isochronal (20 min) annealing effect on the optical absorption spectra of $CdS_{0.4}Se_{0.6}$ (a) and $CdS_{0.22}Se_{0.78}$ (b) nanocrystals after X-ray irradiation with 3240 Gy (a) and 270 Gy (b).

The samples of $CdS_{0.22}Se_{0.78}$ and $CdS_{0.4}Se_{0.6}$ nanocrystals, irradiated with 270 and 3240 Gy, respectively, were chosen for isochronal (20 min) annealing studies, performed after durable storage of the irradiated samples. The initial absorption spectra of $CdS_{1\text{-}x}Se_x$ quantum dots were observed to recover gradually in the temperature range 375–575 K. For $CdS_{0.4}Se_{0.6}$ the increase of the annealing temperature T_a first leads to the reverse, red shift of the absorption edge, and at $T_a > 500$ K the quantum-size-related features gradually begin to reveal. After annealing to 575 K the initial spectrum shape is restored (See Fig. 6, a), though for $CdS_{0.22}Se_{0.78}$ nanocrystals the structure of the lowest-energy confinemen-related features is not restored completely even at $T_a = 643$ K (Fig. 6). Note that the irradiation-induced absorption increment in the glass matrix itself is also annealed within the range of 375–575 K.

Generally, several factors can be responsible for the observed behaviour of $CdS_{1\text{-}x}Se_x$ nanocrystals absorption spectra under X-ray irradiation and annealing. The gradual smearing of the size-quantum features, observed for both samples, can be attributed to the X-ray induced ionization of the quantum dots due to electron (hole) transfer between the nanocrystals and irradiation-activated electron (hole) traps in the host matrix. With the increase of the irradiation dose the transferred charge-carriers occupy the confinement-related levels in the nanocrystals, gradually disabling the lower-energy transitions. Therefore, in $CdS_{0.22}Se_{0.78}$ quantum dots the irradiation-induced changes affect only the lower-energy features. In the case of $CdS_{0.4}Se_{0.6}$ nanocrystals the discussed effect results in the observed blue shift of the absorption edge.

Note that a similar effect (the blue shift of the absorption edge) was observed in CdS nanocrystals under X-ray irradiation [9] and CdSe quantum dots under intense light irradiation [23], though the transformation of the quantum-size-related maxima is not reported in any of the quoted references. In both cases the blue shift is explained by photoionization of the quantum dots, the photoelectrons leaving the microcrystals and being captured by the traps in the glass [9, 23]. However, one should note that, as follows from the results of photoluminescence and ESR studies of X-ray irradiated CdS quantum dots in borosilicate glass, the X-ray induced defects in the quantum dots differ from the photoinduced defects [10].

However, there are at least two more possible explanations for the absorption edge blue shift in the irradiated $CdS_{1-x}Se_x$ nanocrystals. At normal conditions, $CdS_{1-x}Se_x$ quantum dots in borosilicate glass matrix already sustain hydrostatic pressure from the matrix which is caused by the difference in the values of thermal expansion coefficients for the matrix and $CdS_{1-x}Se_x$ [5, 6]. X-ray irradiation can result in the additional hydrostatic pressure upon the nanocrystals due to the known phenomenon of radiation swelling of the glass matrix [24]. However, since the pressure-induced energy gap shift dE_g/dp values for $CdS_{0.22}Se_{0.78}$ and $CdS_{0.4}Se_{0.6}$ nanocrystals embedded in the borosilicate glass are rather close, as follows from our measurements [25], and no blue shift is observed in X-ray irradiated $CdS_{0.22}Se_{0.78}$ samples, one may conclude that the role of additional hydrostatic pressure in this case is negligible.

It should be also noted that, since the host borosilicate matrix in our case contains a considerable (13 mass %) amount of ZnO, the blue shift of the absorption edge can also be related to the incorporation of zinc into the quantum dots where it can substitute Cd, forming quaternary $Cd_{1-y}Zn_yS_{1-x}Se_x$ mixed nanocrystals. Such possibilities are reported to occur at thermal annealing of $CdS_{1-x}Se_x$ quantum dots in Zn-containing silicate glass matrix [3, 26, 27]. However, the completely reversible character of the absorption spectrum variation observed at the post-irradiation annealing excludes the possibility of X-ray induced Zn diffusion from the glass to $CdS_{1-x}Se_x$ quantum dots. Note that the isochronal annealing temperature in our case (below 600 K) is much lower than the temperatures at which zinc diffusion into the nanocrystals is reported (T_a>850 K [26, 27]).

4. Conclusions

XL spectra of $CdS_{1-x}Se_x$ nanocrystals embedded in a borosilicate matrix were measured, the XL band parameters being analyzed with the account of the luminescence of the host matrix itself.

X-ray irradiation is shown to result in the smearing of the quantum-size-related maxima in the absorption spectra of $CdS_{1-x}Se_x$ quantum dots and subsequent absorption edge blue shift. The initial spectrum of the samples is completely restored at annealing in the temperature range 375–575 K. The observed transformation of the quantum-size-related features in the optical absorption spectra of $CdS_{1-x}Se_x$ quantum dots under X-ray irradiation can be attributed to the ionization of the nanocrystals with charge-carrier transfer between the quantum dots and the electron (hole) traps in the host matrix.

Acknowledgment

The authors are much obliged to I.I.Turok for the preparation of the samples.

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