Optical investigations of thermostimulated changes in an ensemble of CdS$_x$Se$_{1-x}$ quantum dots embedded into borosilicate glass matrix

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Abstract. We have employed the absorption and Raman spectroscopies to study thermo-stimulated changes in an ensemble of CdS$_x$Se$_{1-x}$ quantum dots embedded into a borosilicate glass matrix. It is shown that additional annealing of the sample containing CdS$_x$Se$_{1-x}$ quantum dots leads to growth of the new ones with higher Se content and average radius approximately equal to the previous value. The conclusion was made that the new particles were grown due to diffusion of Cd, S and Se atoms from a glass matrix which was still remained in the oversaturated state, i.e. the recondensation growth stage (so-called «Ostwald ripening» or «diffusion-limited aggregation») was not achieved during the annealing process. Some parameters of the dots were determined.

Keywords: nanocrystals, quantum dots, optical absorption, Raman scattering.

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Cadmium-sulfur-selenium colored glasses (cut-off filters) are usually synthesized in two steps [1]. The oversatu-rated solid solution of Cd, S and Se atoms in a borosilicate glass host is obtained by melting of the glass constituents together with the semiconductor ingredients within a range of 1200 to 1300°C. Then CdS$_x$Se$_{1-x}$ nanocrystals are grown by annealing of this solid solution at tempera-tures from 500 to 700 °C, which are high enough to cause effective diffusion of the semiconductor ions in a glass matrix and low enough to maintain solution oversatura-tion. Typical color of the glass is appeared at the anneal-ing and the following three stages are gone on: (1) the nucleation, (2) the growth on account of dissolved mat-ter, and (3) the recondensation growth (the so-called «Ostwald ripening») when the most of Cd, S and Se ions are already taken their places in CdS$_x$Se$_{1-x}$ nanocrystals, and the largest particles are grown at dissolution of the smaller ones. At the last stage an asymmetrical size dis-tribution with the particle concentration ~10^{-15} cm^{-3} is settled [2]. In most cases, the particles of greatest interest for quantum-confinement effect studies have sizes of a few nanometers and the knowledge of their main param-eters (average radius $\bar{r}$, band gap energy E_{g0}, composi-tion x, etc.) becomes of the very actual problem.

In this paper, we report on the additional increase in the number of CdS$_x$Se$_{1-x}$ quantum dots with the higher Se content at the annealing of the sample with the quantum dots which were synthesized before. At the same time, the possibility on determining the composition and the aver-age size of the particles simultaneously from the absorp-tion and the resonant Raman spectra is demonstrated.

The sample containing CdS$_x$Se$_{1-x}$ quantum dots (OS-17 colored cut-off filter glass) was chosen from the com-mercial filter set. Considering the low absorption coeffi-cient ($K_{max} \approx 10$ cm^{-1}) due to the optical transitions be-tween the first quantum-confinement levels ($E_{01}^{h} \rightarrow E_{01}^{e}$) we've concluded the nanocrystal concentration to be the lowest in this glass among all over the rest ones from the set which have typical values of K_{max} from 40 to 60 cm^{-1}. This allowed us to assume that the glass matrix in our sample was still oversaturated before the annealing, i.e. some excess of Cd, S and Se ions remained in the matrix in isolated states, and they could further participate in the nanocrystals growth being subjected to an additional heat treatment. Thus, the sample was heated at 600°C during the different periods of time in the air. Then, the absorption spectra were measured with a standard opti-cal system at room temperature and were analyzed by the method proposed in [3–5]. The color of the sample was essentially changed from the poorly yellow to the brightly red one after the annealing. This could be caused by increasing both of the Se content in nanocrystals

and(or) their sizes. Two typical spectra (before annealing and after annealing during 3 hours) are shown in Fig. 1.

Both spectra in Fig. 1 have typical peaks corresponding to $E_{01}^h \rightarrow E_{01}^e$ optical transitions and centered at ~2.41 eV before the annealing and at ~2.16 eV after it which indicates that electrons and holes are strongly confined in CdS_xSe_{1-x} nanocrystals, and the absorption edge is drastically shifted to the red side. Besides, the value of K_{max} at the absorption peak increases approximately twice after the annealing that can be attributed to the higher optical density of the semiconductor matter in the transparent glass matrix.

The first-order Raman spectra (Fig. 2) were also measured before and after the sample annealing. The nearly «back-scattering» configuration was used with the excitation by Ar^+ laser line ($\lambda = 514.5$ nm).

CdS_xSe_{1-x} is classified in the so-called «two-mode behavior» alloys: CdS-like and CdSe-like longitudinal optical vibrational modes (LO), characteristic of the binary compounds CdS and CdSe, are simultaneously present at each intermediate concentration. Both the spectral position of the LO phonon lines and the relation between their intensities are dependent on a semiconductor composition. The CdSe-like LO modes (at 202.3 cm^{-1} before the annealing and at 204.8 cm^{-1}, after the annealing) and the CdS-like LO modes (at 290.2 and 283.7 cm^{-1}, correspondingly) are the most intense lines in the spectra of our sample. The relation between the intensities of CdSe- and CdS-like modes (I_{CdSe}/I_{CdS}) is about 0.84 before the annealing being considerably changed to $I_{CdSe}/I_{CdS} \approx 1.33$ after it which clearly suggests the increasing of the Se content in semiconductor *phase*. The halfwidths of the LO peaks are also increased at the annealing (see Table 1).

The model of optical transitions [3, 4] enables us both to calculate the absorption spectra and to estimate simultaneously $\bar{r}$, E_{g0} and x parameters of CdS_xSe_{1-x} quantum dots with sufficiently high accuracy. Thin solid curves in

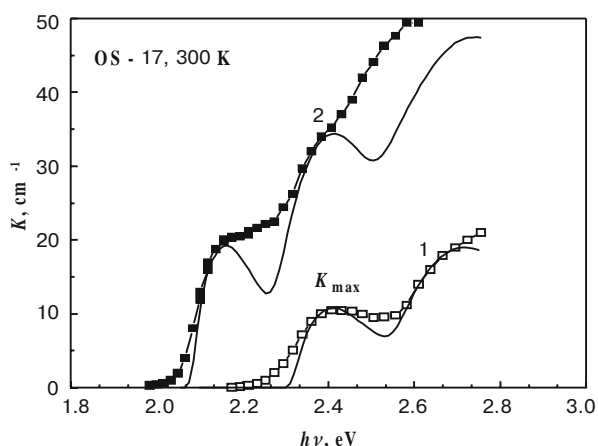**Fig. 1.** Absorption spectra of CdS_xSe_{1-x} -doped glass before (1) and after (2) annealing at 600 °C during 3 hours in the air. Solid lines represent the best fit by the model [4] to the experimental data (dots).

Fig. 1 represent the calculated spectra. The average radii of nanocrystals and their band gap energies E_{g0} (Table 1) were estimated as the fitting parameters taking into account the matrix pressure effects [6]. The nanocrystal composition was then extracted from the dependence of $E_{g0}(x)$, which is well-known for the bulk crystals. Note that E_{g0} value obtained as a fitting parameter in the aforementioned calculation procedure corresponds to the gap of the bulk, i.e. the confinement energies of the electrons and holes are already subtracted from E_{g0}.

One can conclude from Table 1 that the annealing drastically changes the composition in an ensemble of quantum dots when increasing the Se content, while the average radius of nanocrystals is only risen from 2.45 to 2.70 nm according to the absorption data, i.e. approximately by 10%. These data correlate well with the fact that the form of the absorption edge is not essentially changed under the annealing, while the red shift of the

Table 1. Values of the CdS_xSe_{1-x} quantum dots parameters obtained by fitting the calculated absorption spectra to the experimental ones and by analysis of the Raman spectra.

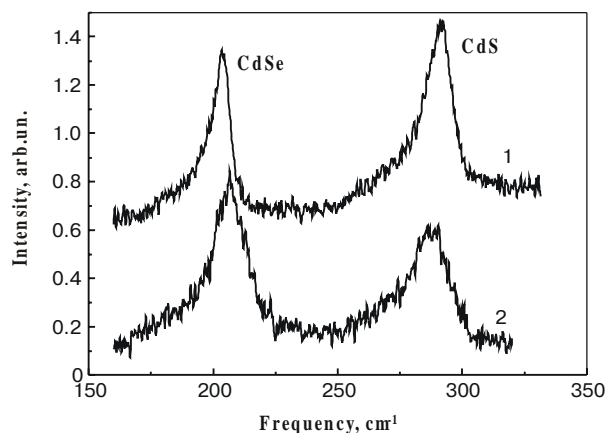| Parameter	Before annealing	After annealing
$\bar{r}$, nm	2.45 ±0.05	2.70 ±0.05
X (absorption)	0.75 ±0.05	0.42 ±0.05
X (Raman scattering)	0.65 ±0.03	0.38 ±0.03
E_{g0}, eV, 300 K	2.090 ±0.002	1.895 ±0.002
ν_1, cm^{-1} (CdSe)	202.3 ±0.1	204.8 ±0.1
ν_2, cm^{-1} (CdS)	290.2 ±0.1	283.7 ±0.1
Γ_1, cm^{-1} (CdSe)	12.5	16.7
Γ_2, cm^{-1} (CdS)	13.1	21.8

Fig. 2. First-order Raman spectra of CdS_xSe_{1-x} – doped glass before (1) and after (2) annealing at 600 °C during 3 hours in the air.

edge consists of about 0.24 eV. The composition estimated as it was proposed in [3, 5] correlates well with the absorption spectroscopy data.

Thus, the annealing of the sample at 600 °C during 3 hours in air increases the average radius of CdS_xSe_{1-x} quantum dots insignificantly, while it increases essentially (~30%) the Se content in the semiconductor *phase* of the matter. Taking into account this fact and the peculiarities observed in absorption and Raman spectra we have concluded that the initial glass contains CdS_xSe_{1-x} quantum dots with $x = 0.65$-0.75 and $\bar{r} = 2.45$ nm. After annealing, the number N of quantum dots is increased at least twice that is suggested by the rise of K_{max} value ($K_{max} = \sigma N$, where σ is the cross section of the absorption, and N is the number of absorptiion centers) practically without visible changes of the shape of the absorption edge. Such increase of the dot quantity can only take place when the glass matrix of the initial sample contains Cd, S and Se in atomic-molecular state simultaneously with the CdS_xSe_{1-x} dots ($x = 0.65$–0.75), i.e. the matrix oversaturation is not still equal to zero [1]. The observed value of the insignificant increasing of the quantum dots average radius argues us that the recondensation growth stage (Ostwald ripening), when the largest dots are grown through dissolution of the smaller ones was not achieved during the annealing. At the same time, an essential increase of the Se content in the semiconductor *phase* without visible changes of the average radius in the *ensemble* of nanocrystals can be explained by appearance of the new ones with the higher Se content. This conclusion is also suggested by increasing LO peaks halfwidth in Raman spectra (Table 1 and Fig. 2), which can be explained by superposition effect from the dots having different composition, i.e. large composition dispersion is appeared in the sample at such annealing, and the x values are determined by optical methods only as the averaged ones through the whole ensemble of the dots.

These data correlate well with the ones presented in [7], where the conclusion was made from x-ray and chemical data that the behavior is typical for the Se ions to remain in the glass host while the S ions more easily takes their places in the nanocrystal lattice of CdS_xSe_{1-x} quantum dots. Therefore, one can consider that the growth of CdS_xSe_{1-x} quantum dots in the glass matrix by the process of diffusion-controlled phase decomposition of the oversaturated solid solution during both the nucleation stage and the growth on account of dissolved matter one proceeds as follows: the dots containing mainly S atoms (with the ionic radius of about 0.184 nm) are grown at the first time of the process while the Se atoms (with the ionic radius of about 0.198 nm) are taken their places in the lattice sites at more later stages that leads to the composition dispersion.

In the framework of this model, one can consider that the absorption peak in the spectrum of the initial (*unannealed*) sample (Fig. 1, curve 1) is caused by optical transitions $E_{01}^h \rightarrow E_{01}^e$ in CdS_xSe_{1-x} quantum dots with $x = 0.65$–0.75, while the same peak in the spectrum of the *annealed* sample corresponds to the same transitions but in the dots with $x = 0.38$–0.42. So, two types of quantum dots with the different Se content are present in the sample as the result of the repeated additional heat treatment. From the relation of K_{max} values before and after the annealing we have concluded that the concentration of CdS_xSe_{1-x} quantum dots with $x = 0.38$–0.42 additionally grown in the glass at the annealing exceeds the initial concentration of the dots with $x = 0.65$–0.75 approximately in double time.

Acknowledgements

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