Spectral dependence of the optical absorption temperature coefficient of $CdS_{1-x}Se_x$ nanocrystallites embedded in a silicate glass

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ABSTRACT

The absorption temperature coefficient of $CdS_{1-x}Se_x$ nanocrystallites embedded in a silicate glass has been studied in the temperature range above room temperature at different technological regimes and sizes of nanocrystals. To understand the optical properties of silicate glasses with semiconductor nanocrystallites, especially that at the initial stage of their formation, it is necessary to include the structural changes occurring in the nanocrystals during the heat treatment.

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1. Introduction

Semiconductor $CdS_{1-x}Se_x$ quantum dots (QDs) embedded in a silicate glass matrix has attracted considerable attention over the past years because of their novel optical and dynamical properties associated with the quantum confinement effects [1–3]. Such silicate glasses span the visible region of the spectrum and can be used in developing new optoelectronic devices, for example, optical filters, optically bistable elements, switches, modulators, light emitting diodes and so on [4–7]. These systems have been also intensely researched for their large and tuneable third order nonlinearity near the band edge [8]. In the recent years optical linear and non-linear spectroscopy, high resolution transmission electron microscopy [9–11], micro-Raman and X-ray diffraction experiments [1,12–13] have been carried out with the aim to understand the dependence of the optical and electrical properties of such composite materials on the QD average size and size (shape) distribution.

The optical properties of silicate glasses containing semiconductor nanocrystallites are controlled by their mean size and size distribution. Particularly, the dependence of the optical absorption edge on the nanocrystal size is explained in terms of the quantum size effect in nanocrystals. However to understand more in detail the optical properties of silicate glasses with semiconductor nanocrystallites, especially the properties at the initial stage of their formation, it is necessary to also include the structural changes occurring in the nanocrystals.

The aim of this study is the effect of the structural changes in semiconductor $CdS_{1-x}Se_x$ nanocrystallites occurring during their heat treatment on the optical properties of silicate glasses containing them. For this purpose, we studied the behaviour of the absorption temperature coefficient of $CdS_{1-x}Se_x$ nanocrystallites embedded in a silicate glass at different technological regimes and having different average size.

The samples have been grown using the standard glass technology. The total amount of semiconductor constituents (CdS and CdSe) in the initial batch was about 1% in weight. The melting process was carried out at temperatures of 1350–1400 °C. After the fast cooling of the melt, a supersaturated solid solution is formed. During the last heat treatment the disintegration process starts, resulting in a fluctuational formation of semiconductor nanocrystallites [12].

2. Experimental results and discussions

The transmission and reflectance spectra of the samples have been measured in the temperature range of 20–400 °C, where the changes in the sample temperature lead only to the reversible changes in the optical band gap and coloration of the samples.

The optical absorption coefficient K at a fixed wavelength of the samples varies almost linearly with the temperature. Such dependence for one of the samples is presented in Fig. 1. The optical absorption temperature coefficient dK/dT, determined for different wavelengths, has different behaviour in the short and long wavelength parts of the spectrum. The close inspection shows that the dK/dT being positive in long wavelength region becomes negative for the short wavelengths of excitation. In Fig. 2 the

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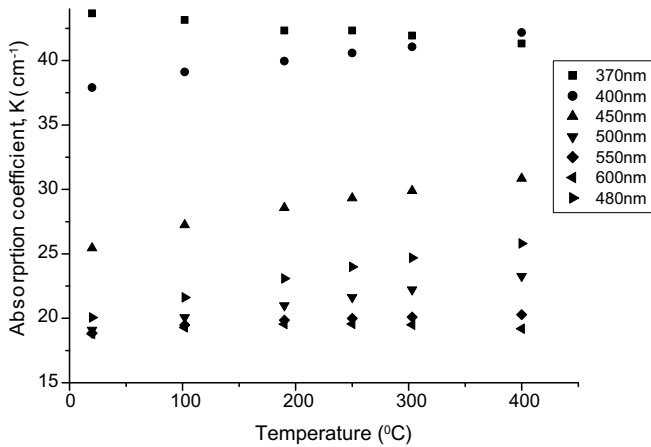 E-mail address: spetrosyan@rau.am (P. Petrosyan).

Fig. 1. Temperature dependence of the absorption coefficient at a fixed wavelength for one of the samples.
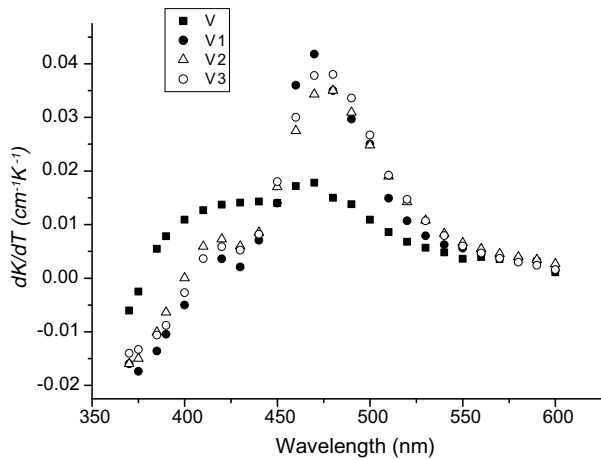

Fig. 2. Wavelength-dependence of the optical absorption temperature coefficient for the samples V after the two steps heat treatment.

wavelength-dependence of the optical absorption temperature coefficient is presented for the sample subjected to the two steps heat treatment – short (5 min) at 560 °C and successive long heat-treated at 400 °C. The different curves correspond to different durations of the heat treatment at 400 °C. Here the curve V correspond to the sample without any heat treatment at 400 °C, while the curves V1, V2, and V3 correspond to the samples subjected to the heat treatment at 400 °C during the 1.11, 2.5 and 3.67 h, respectively. It is seen that the later heat treatment at 400 °C causes the appearance of distinctive maxima at the wavelengths 415 and 470 nm.

Such behaviour of the optical absorption temperature coefficient can be attributed to the interband optical transitions between quantum-size energy levels in nanocrystallites, appearing in the glass matrix after the heat treatment. Throughout the whole discussion it will be assumed that the composition of the crystallites is governed mainly by the initial amount of semiconductor constituents and is independent on heat treatment time [16]. The electron microscope studies [14,17,18] show that the crystalline structure of nanocrystals is formed gradually and takes its final state during the sufficiently long heat treatment. At the first stage of the heat treatment, a controlled structure formation takes place but the ordered crystal lattice is not completely formed, which is confirmed by the fact that not all of crystallographic surfaces show reflection in the electrograms. At the second stage, the reflection in the electrograms is seen from all the crystallographic surfaces but the

maxima are still not a well developed. A further heat treatment leads to the narrowing of the diffraction rings, which is an indication of the final formation of ordered crystalline lattice. The nanocrystallite energy gap is vague until the crystal lattice is completely formed. The process of the crystalline structure formation and appearance of the corresponding energy gap is also manifested by the appearance of peaks in the spectral dependence of the temperature coefficient of the optical absorption. In particular, the spectral peaks of dK/dT observed at 415 and 470 nm (Fig. 2) can be explained by formation of the two lowest discrete energy levels in nanocrystallites.

A different sign of dK/dT in the short and long wavelength parts of the absorption spectra reflects the change with the temperature in the electron population degree of different energy levels in the crystallite conduction band. The increase in temperature, causing the electron transfer to the higher energy levels and, hence, leading to the higher population degree of upper states and lower population degree of ground state, will results in an increase of the interband absorption coefficient in the long wave range and will reduce it in the short wave range of the spectrum in accordance with the experimentally observed transmission spectrum.

Fig. 3a and b presents the spectral dependences of the absorption temperature coefficient for the samples subjected to the heat treatment at 560 °C (the duration of the treatment for the samples P, Q, R, S, T and U was, respectively, 3.33, 11.7, 21.7, 30, 43.3 and 106.7 min). As it is seen the increase in the heat treatment time results in the formation of the maxima in the spectrum of the optical absorption temperature coefficient, which are shifted with treatment time to the longer wavelength part of the spectrum and
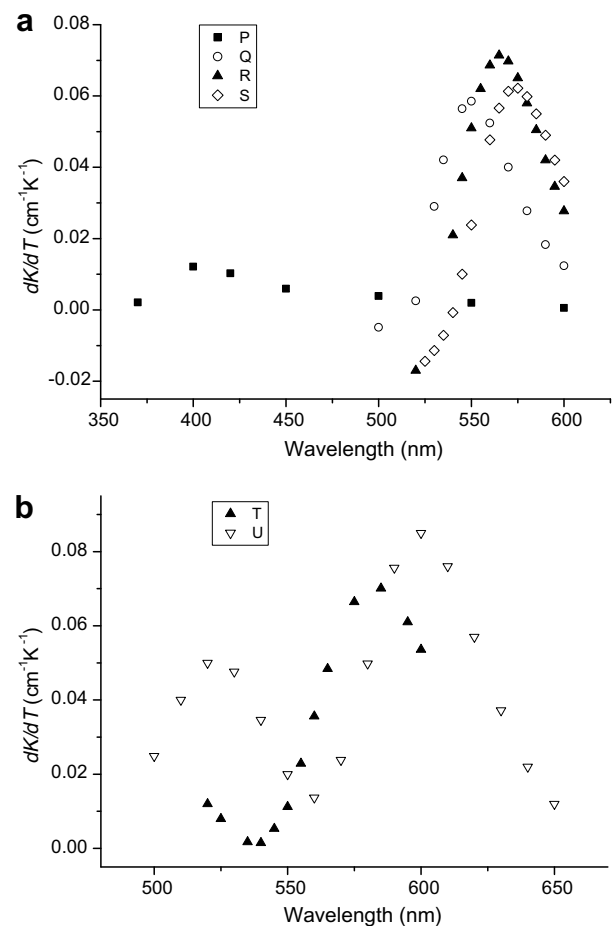

Fig. 3. The spectral dependences of the absorption temperature coefficient for the samples: (a) P, Q, R, S and (b) T, U.

the longer the sample has been heat-treated, the larger is the peak value of the wavelength-dependence of dK/dT. It is worth noting that the second maximum appears for the samples which have been subjected to more than 40-min heat treatment. This maximum lies in the short-wavelength range of the spectrum (see Fig. 3b). The observation of the two peaks in the spectral dependence of the temperature coefficient of the optical absorption cannot be connected with the separate formation of the nanocrystals CdS and CdSe. The first reason is that the studied samples differ from each other only by the heat treatment time. As it was mentioned above the raise of the heat treatment time can cause only an increase in size of the nanoinclusions and in their crystal lattice perfection. Hence, these two maxima must be observed in those samples which were heat-treated for a shorter period. The second reason is that the 520 nm and 600 nm wavelengths correspond to the two maxima for the U-sample, respectively. For the case of bulk semiconductors the band gap energy of the CdS and CdSe at room temperature are 2.42 eV (480 nm) and 1.72 eV (698 nm), respectively. Size quantization can lead only to the shift of the absorption edge towards the short wave range of the spectrum. In this case the first maximum had to be in the range of waves shorter than 480 nm. And finally, the Raman spectroscopy study of the samples, carried out by us [10], shows that there is only a single CdS$_{1-x}$Se$_x$ ($x = 0.6$) phase in the silicate glass matrix.

It was also confirmed that in the growth process the shape of the formed inclusions changes from spherical to hexagonal prism. [19,10]. For the absorption temperature dependence the experimental results have been interpreted in accordance with a model, developed by Wu and co-workers [15], for the interband optical absorption coefficient of a non uniform semiconductor quantum dot system, with a size distribution described by a Gaussian function. Within this model the averaged absorption coefficient of nanoparticles with cubic shape and average side length a_0 can be expressed as

$$K = \frac{\beta}{a_0} \sum_{n^2} \frac{g(n^2)}{\xi n^2} e^{\frac{(n/x - 1)^2}{2\xi^2}} \tag{1}$$

where $\beta = \frac{1}{\sqrt{2\pi}} \left(\frac{A\mu}{\pi^2 \hbar^2} \right)$ is a dimensionless coefficient, $A = \frac{2\pi e^2 |P_n|^2}{m_0^2 \varepsilon_r^{1/2} \epsilon_0 c w}$, P$_n$ is the momentum matrix element, ε_r is the dielectric constant of the host material, $g(n^2)$ is the degeneracy of dot energy levels determined by $n^2 = \sum_i n_i^2 (i = 1, 2, 3 \ldots; n_i = \pm 1, \pm 2, \pm 3 \ldots)$, $\xi = \frac{D}{a_0}$, $D = \sqrt{\langle (a - a_0)^2 \rangle}$ is the standard deviation, $x^2 = \frac{hw - E_g}{\pi^2 \hbar^2 / 2\mu a_0^2}$ (where E$_g$ is the energy gap of the bulk material, and $\mu^{-1} = \frac{1}{m_e^*} \frac{1}{m_h^*}$ is the reduced mass of an electron-hole pair).

For the simplicity of discussions we used above the model of cubic dots, but, of course, real dots may have other geometrical forms and energy levels quantum numbers. Therefore the results, presented here have only qualitative meaning and can differ from that, for example, for spherical quantum dots by some numerical factors.

From above expression for K, the spectral dependence of the absorption temperature coefficient has been calculated, $\frac{dK}{dT} = \frac{dK}{dE_g} \frac{dE_g}{dT}$. As $\alpha = \frac{\partial E_g}{\partial T}$ can be taken as a constant parameter in the measured temperature range and is known from the experiments, we have

$$\frac{dK}{dT} = \frac{dK}{dE_g} \alpha = \frac{dK}{dx} \frac{dx}{dE_g} \alpha = \frac{\beta \alpha}{a_0} \sum_{(n^2)} \frac{g(n^2)(n/x - 1)}{\xi^3 n} e^{-\frac{(n/x - 1)^2}{2\xi^2}} \frac{dx}{dE_g}$$

$$= -\frac{\beta \alpha \sqrt{\mu}}{\sqrt{2\pi} \hbar \sqrt{hw - E_g}} \sum_{(n^2)} \frac{g(n^2)(n/x - 1)}{\xi^3 n x^2} e^{-\frac{(n/x - 1)^2}{2\xi^2}} \tag{2}$$

When calculating the spectral dependences of the absorption temperature coefficient, only four lowest levels in nanocrystals has been taken into consideration ($n^2 = 3, 6, 9, 11$). The experimental spectral dependences of the absorption temperature coefficient have been best fitted using Eq. (2) with $E_g = 1.85$ eV.

Using the results from above model the mean nanocrystallite size for the sample V3 can be estimated to be about 2.48 nm, while the same size estimated from the absorption edge energy is about 1.8 nm.

In Fig. 4 we report the spectra and the best fit for some representative samples. The a_0, β, ξ values found from the best fitting and the energy of the optical absorption edge E_g (QD) for different samples are given in Table 1.

We can see from Table 1 that the increase of the heat treatment duration leads to nanocrystallites of greater size.

The mean size of the nanocrystallites a_0 can be also estimated from the energy of the optical absorption edge, using the expression:

$$E_g(\text{QD}) = E_g + E_R \left(\frac{R_B \pi}{a_0} \right)^2 \tag{3}$$

where R_B is the exciton Bohr radius in a bulk material, and E_R is the Rydberg constant. In Fig. 5 we report the mean size of nanocrystal-
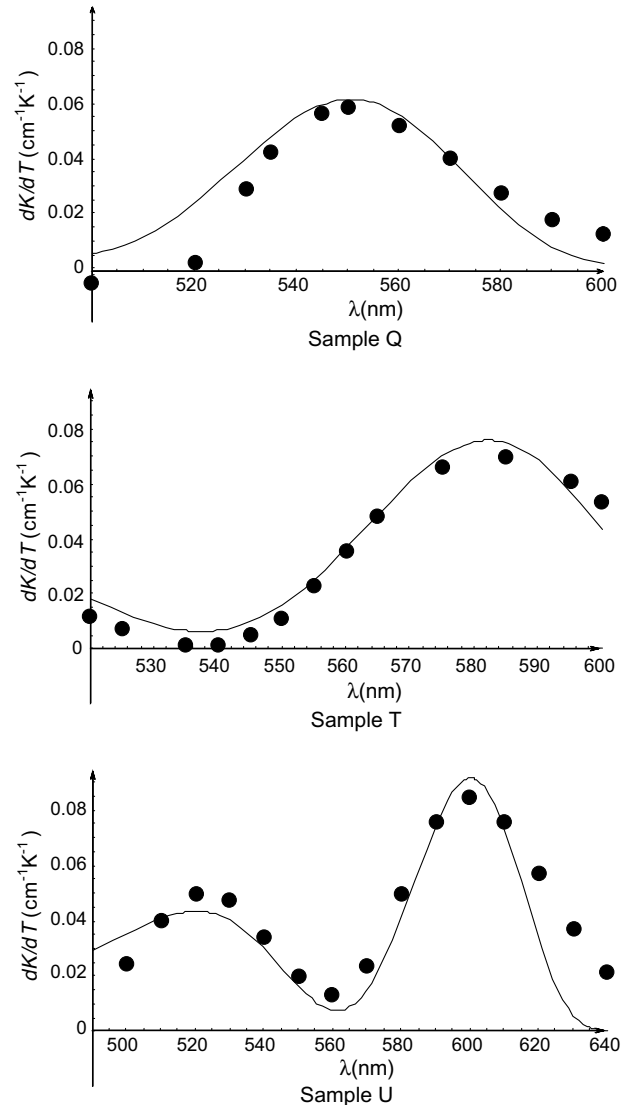

Fig. 4. The best fit of calculated from Eq. (1) spectral dependence of the absorption temperature coefficient (continuous line) with the experimental data (circles) for some representative sample.

Table 1
The estimated parameter values for different samples

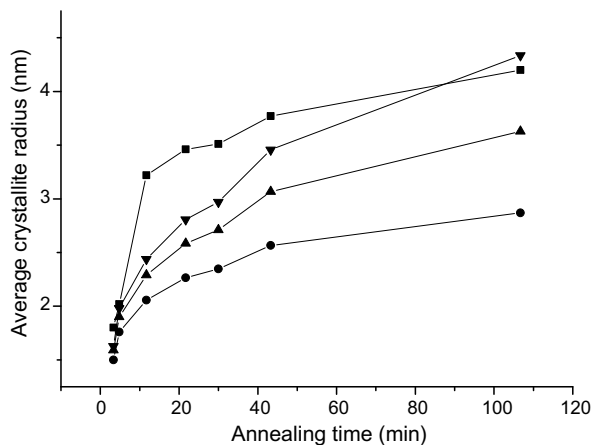| Sample	a_0 (nm)	β	ξ	E_g (QD) (eV)
P	1.8	0.1×10^{-5}	0.2	2.78
V	2.02	0.3×10^{-5}	0.25	2.51
V1	2.4	0.18×10^{-5}	0.14	–
V2	2.46	0.16×10^{-5}	0.139	–
V3	2.48	0.16×10^{-5}	0.138	–
Q	3.22	0.23×10^{-5}	0.155	2.32
R	3.46	0.290×10^{-5}	0.155	2.229
S	3.49	0.290×10^{-5}	0.155	2.199
T	3.77	0.285×10^{-5}	0.155	2.134
U	4.2	0.295×10^{-5}	0.155	2.067

Fig. 5. Calculated from Eq. (2) mean size of the nanocrystallites as a function of heat treatment time at 560 °C for different values of bulk material band gap energy E_g (● E_g = 1.85 eV, ▲ E_g = 1.9 eV, ▼ E_g = 1.95 eV). The values of the average size of the nanocrystals derived from wavelength-dependence of the absorption temperature coefficient (Table 1) are also shown (with symbol ■).

lites for the samples treated at 560 °C, as a function of the heat treatment duration, using different values for the band gap energy of the bulk material (● E_g = 1.85 eV, ▲ E_g = 1.9 eV, ▼ E_g = 1.95 eV). In the same figure we show (with symbol ■) the mean size of the nanocrystallite shown in Table 1, (the values defined from spectral dependence of the optical absorption temperature coefficient). It is seen that if for E_g we use the same value, i.e. 1.85 eV, the mean size of nanocrystallites is determined from the absorption edge is approximately 1.5 times smaller than that found from the spectral dependence of the absorption temperature coefficient. In order to get nearly the same value for the average sizes, a larger value for the bulk band-gap energy, E_g = 1.95 eV, should be used in Eq. (3). The reason for such larger values for the bulk band-gap energy is not clear yet. It could be explained by the fact that the nanocrystallites in the glass matrix heat treated for different durations may have different degree of crystalline perfection and therefore different values of absorption edge. At present we are developing a theoretical model to explain a band structure transformation of nanocrystallites during the process of crystal lattice formation and the results will be published elsewhere.

The data presented in Table 1 also show that the heat treatment at 560 °C reduces the relative standard deviation of the dot size, ξ, and the main decrease occurs at the first stage of the heat treatment. Similar behaviour of ξ is seen also for the samples heat-treated at 400 °C. The change in ξ at such low temperature of heat treatment can not be caused by the very slow diffusion growth process. Note a decrease of ξ has the similar effect on the absorption temperature coefficient as the nanocrystallite formation.

3. Conclusions

The absorption temperature coefficient of $CdS_{1-x}Se_x$ nanocrystallites embedded in a silicate glass has been studied in the temperature range above room temperature. The temperature dependence of the absorption coefficient has been shown to be linear at a fixed wavelength. The electron redistribution between the energy levels in the conduction band of nanocrystals with increasing temperatures can lead to a different sign of dK/dT in the short and long wavelength parts of interband absorption spectra. Low temperature (400 °C) heat treatment without causing diffusion growth of nanocrystallites, leads to the appearance of well resolved maxima in the spectral dependence of the absorption temperature coefficient. Such behaviour of the absorption temperature coefficient can be attributed to the increasing crystalline perfection of semiconductor nanoparticles, occurring during the low temperature heat-treatment of the samples.

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