Mechanism of photoinduced luminescence degradation in CdS$_X$Se$_{1-X}$ quantum dots

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Abstract. A possible mechanism of the photoinduced luminescence degradation in the hexagonal CdS$_X$Se$_{1-X}$ quantum dots synthesized in a glass matrix is discussed using luminescence decay kinetic investigations and *ab initio* calculations of chemical bond energies at the boundary between CdSe cluster and SiO$_X$ fragment. The mechanism implies that the photoinduced break of Se-O bonds increases the electric field inside a quantum dot, which stimulates diffusion of the cadmium vacancy to the surface. This mechanism enables to explain the luminescence photodarkening effect in quantum dots as well as the degradation of the nonlinear optical device parameters.

Keywords: quantum dots, photodarkening effect, photoluminescence.

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Several features are related to the photodarkening effect that is experimentally observed in CdS$_X$Se$_{1-X}$ quantum dots in a borosilicate glass matrix [1–10] when subjected to light. They are: (a) the photoluminescence degradation at the light intensity exceeding 0.1–1.0 W/cm^2, (b) changes of the refraction ($\Delta n \sim 8 \times 10^{-7}$ [8]) (c) the increase of the absorption ($\Delta K \sim 0.05$–0.1 cm^{-1}) in the transparency range near the fundamental absorption edge [8], (d) the reduction of the Kerr susceptibility [3] as well as (e) the nonlinear response time [3] and (f) the carrier lifetime [3].

A mechanism of the photoluminescence degradation is not completely established. It was supposed the effect is caused by the photochemical reactions [1] or by the quantum dot photoionization [11], and/or by increasing number of nonradiative recombination centers at the quantum dot surface [4]. Great interest to the effect is motivated by the necessity to clarify the reasons of degradation both the photoluminescence and the nonlinear optical device parameters. This work is aimed to substantiate a possible mechanism of the photoluminescence degradation in CdS$_X$Se$_{1-X}$ quantum dots with the average radius $\bar{r}$ comparable to the Bohr exciton radius in the bulk.

CdS$_X$Se$_{1-X}$ quantum dots with the average radius $\bar{r} = 2.9$ nm synthesized in a borosilicate glass matrix were investigated. Photoluminescence was registered in the standard "reflection" geometry. Ar+ laser with 514.5 nm

light wavelength was used for both photoluminescence excitation and photoinduced annealing of the samples, i.e. to produce photodarkening. Photoluminescence spectra were recorded at the relatively low excitation intensities ($I_t \sim 0.05$–0.5 W/cm^2). The excitation intensity was risen up to $I_t < I_0 < 10^3$ W/cm^2 when the annealing was carried out. The kinetic dependencies of the photoluminescence degradation were recorded at various excitation intensities in the above range. Depending on the excitation level, the characteristic decay times could be changed from several seconds up to several tens of minutes.

At low excitation level (~ 0.05 W/cm^2) three bands are registered in the spectra of the initial (unannealed) samples (Fig. 1). Two of them (at 1.34 eV and 1.99 eV) correspond to the transitions of free electrons from the quantum confinement levels in a conduction band to the deep (0.56–0.60 eV) and shallow (0.24–0.26 eV) acceptor levels generated inside the band gap by the cation vacancy (V_{Cd}) or by the complex AM_i, where A is V_{Cd}, and M_i are the interstitial atoms of Cd [12]. The nature of the band at 1.57 eV is not ascertained authentically. The direct electron-hole luminescence band at 2.21 eV is clearly shown in the spectra at the excitation levels upper than 0.1 W/cm^2. After photodarkening, the intensity of the acceptor photoluminescence bands is decreased by 90–95 %, while the direct electron-hole luminescence is only decreased by 10–15 %, and it dominates in photodarkened spectra (Fig. 1).

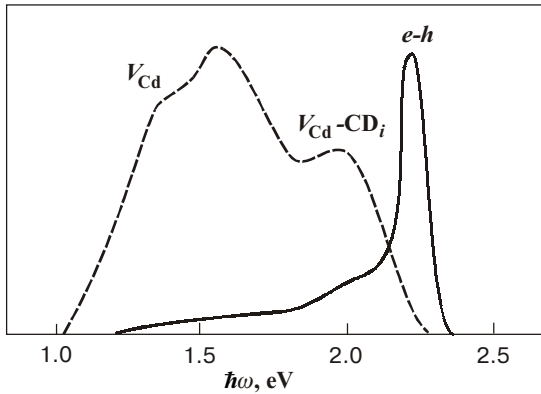**Fig. 1.** Photoluminescence spectra of $CdS_{0.32}Se_{0.68}$ quantum dots ($\bar{r}$ = 2.90 nm) recorded at the excitation intensity 0.5 W/cm^2 and 77 K before (dashed line) and after (solid line) photoannealing for 0.5 hour at the light intensity 60 W/cm^2.

A kinetics of the photoluminescence degradation $I_{PL}(t)$ have a complicated nature (Fig. 2*a*). In most cases, it can be satisfactorily described by the exponential law:

$$I_{PL}^{*}(t) \sim A + B\exp(-t/t_1) + C\exp(-t/t_2) \qquad (1)$$

with two characteristic decay constants t_1, t_2. In (1) A, B and C are the constants depending on a type of the samples and the excitation conditions. In a number of cases the empirical dependence $I_{PL}(t)$ has more complicated character, and its decomposition by only two exponents is unsatisfactory. Therefore, to analyze the dependence of the photodarkening efficiency on the light intensity, it is convenient to use the parameter $\bar{\tau}$ determined as follows:

$$\bar{\tau} = \frac{1}{I_{PL}^{\max}} \int\limits_{0}^{\infty} I_{PL}(t)dt , \qquad (2)$$

where $I_{PL}^{\max}$ is the initial photoluminescence signal measured before photodarkening. In fact, the top integration limit is determined by the time when the degradation process is already saturated. The introduced parameter $\bar{\tau}$ characterizes the time of the nonequilibrium process, and it is determined, as a matter of fact, by the full area between the curve $I_{PL}(t)$ and the line corresponded to the residual photoluminescence signal after photodarkening. In fact, $\bar{\tau}$ is the measure of the photodarkening efficiency.

The characteristic feature discovered from the analysis of the kinetic curves family $I_{PL}(t)$ is the presence of two well-defined exponential parts in the dependence $\bar{\tau}(I_0)$, see Fig. 2*b*. On the first part where the degradation process goes slowly at $0 < I_0 < 10^2$ W/cm^2, $\bar{\tau}$ is sharply decreased when I_0 is increased. On the second part where the process goes effectively at $I_0 > 10^2$ W/cm^2, $\bar{\tau}$ is weakly dependent on I_0. Note, that $\bar{\tau}$ is decreased when the quantum dot average radius is decreased. This feature evidences that the mechanism of the photolumi-

nescence degradation is connected with the process that is saturated at the growth of the light intensity. In the model proposed here, the process is associated with the photoinduced break of Se-O and S-O bonds (their number is limited) at the anion facet of the hexagonal quantum dot. We have also taken into account the fact that the hexagonal quantum dots are synthesized in a glass matrix in the form of a hexagonal prism, which is clearly confirmed by the scanning electron microscopy (SEM) data. The anion facet of the hexagonal prism is charged negatively and the cation facet is charged positively. As the dots are synthesized in oxide glass containing 60–70 % SiO_2, the most part of the anions and cations are presumably bonded with the oxygen and silicon atoms in glass, i.e. the most probable chemical bonds at the quantum dot surface are: Cd-O, Se (S)-O, Cd-Si and Se(S)-Si. Among this binary chemical compounds, only the cadmium silicide is not discovered in the nature [13].

To simulate a charge condition at the anion and cation facets of a quantum dot and to calculate the energies of
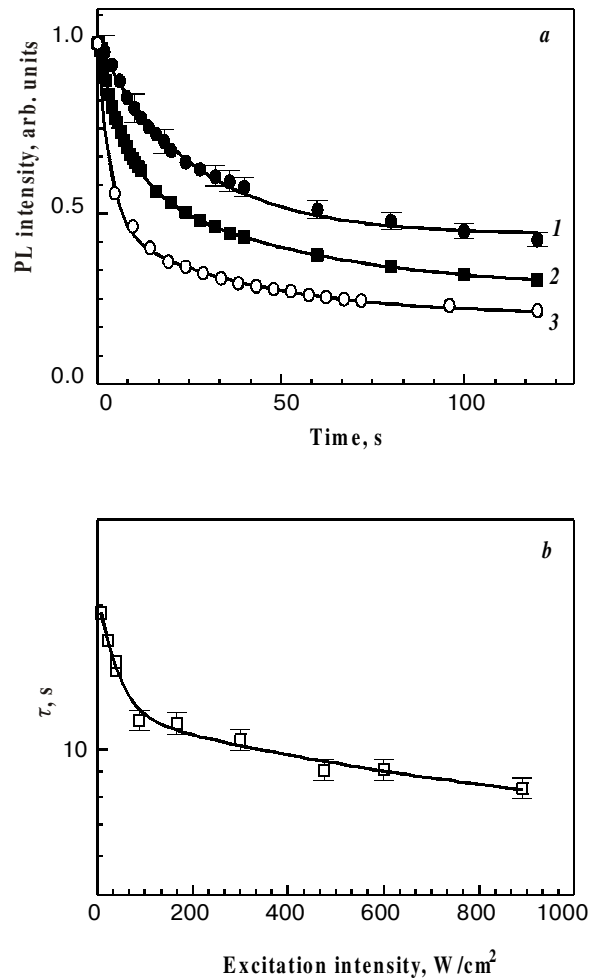

Fig. 2. Typical photodarkening kinetics of $CdS_{0.32}Se_{0.68}$ quantum dots ($\bar{r}$ = 2.9 nm) at the excitation intensities: *a* – *1* – 7.3, *2* – 20.9, *3* – 166.6 W/cm^2. *b* – the dependence of $\bar{\tau}$ on the light intensity.

the above chemical bonds, CdSe hexagonal cluster associated with SiO_X fragment was considered (Fig. 3). *Ab initio* calculations of the chemical bond energies for Cd-O, Se-O, Cd-Si and Se-Si bonds (Fig. 4) and the lines of the electrical potential in the cluster were calculated within the framework of the self-consistent Hartree-Fock scheme by means of the semiempirical PM3 method in the approximation of NDDO (Neglect of Diatomic Differential Overlapping). The calculations have shown that the greatest energy belongs to Se-O (109.9 kcal/mol) and Cd-O (123.5 kcal/mol) bonds at the equilibrium distances between atoms 1.6 and 2.0 Å, accordingly. Moreover, the values of charges induced at the anion and cation facets of the cluster are changed with approaching the oxygen atoms: the positive charge at the cation facet is increased and the negative charge at the anion facet is decreased (Fig. 5). This data evidence that the most probable bonds on the boundaries between the CdS_XSe_{1-X} quantum dot and the glass matrix are the Cd-O and Se-O bonds, and their formation or break changes the values of the charges at the anion and cation facets as well as the difference of the potentials between the facets.

The principal grounds of the mechanism are: (a) the hexagonal quantum dot with the partially ion type of the
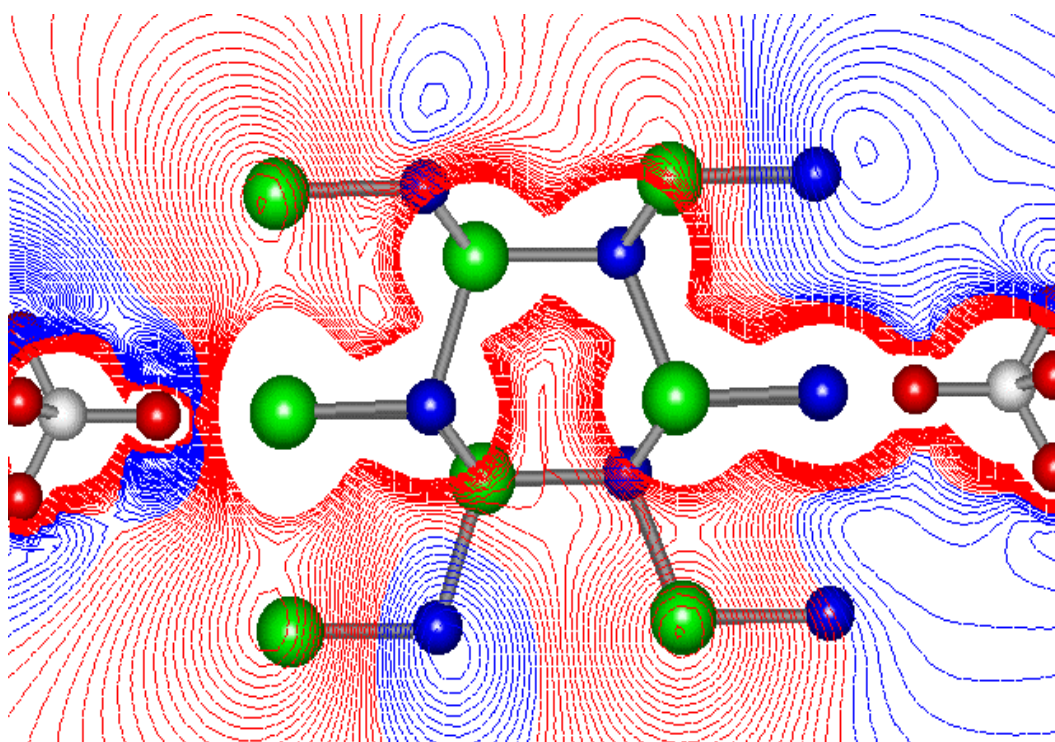

Fig. 3. Hexagonal cluster $(CdSe)_n$ with the lattice parameters: $a = 4.2$ A and $c = 7.01$ A, and SiO_X fragments. Equapotential lines are shown from $-0.2(e/a_B)$ to $+0.33(e/a_B)$ with the step of 0.01, where e is the electron charge.
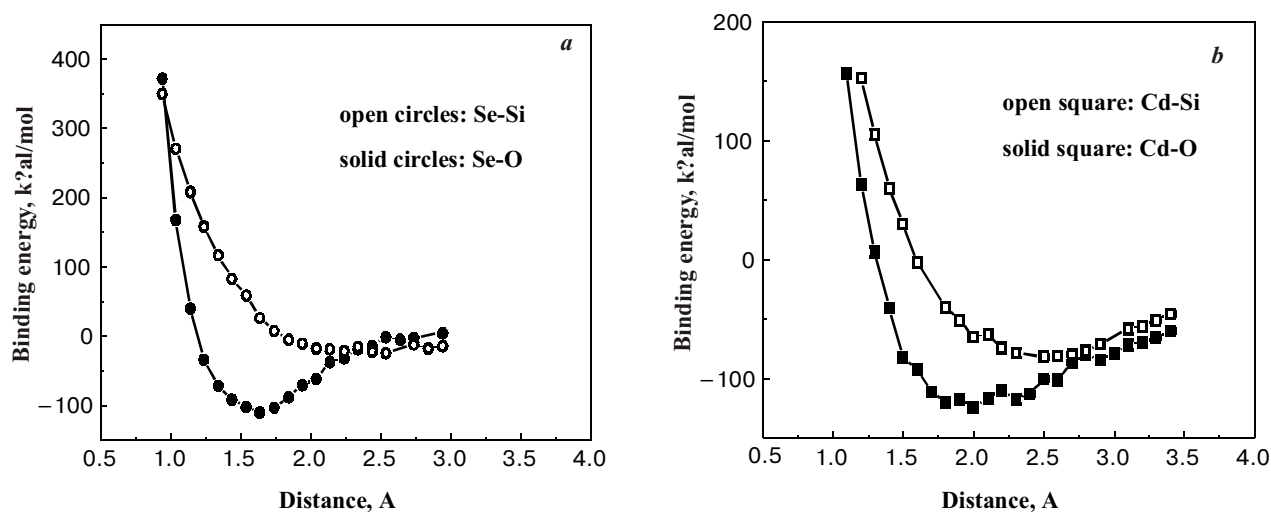

Fig. 4. The bonding energies for Cd-O, Cd-Si, Se-O, Se-Si *vs* the distance between the atoms.
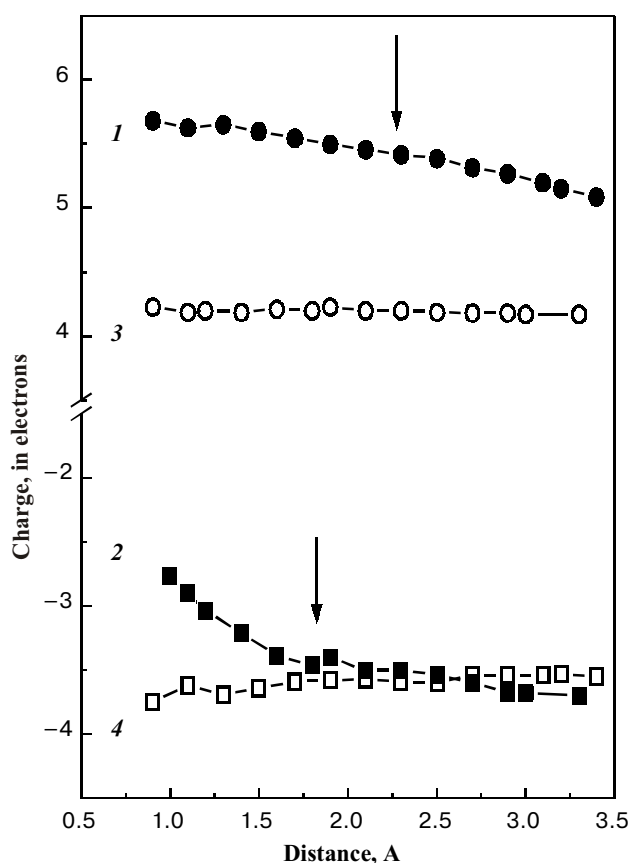
Fig. 5. The induced charges at Cd (*1*) and Se (*2*) facets in CdSe quantum dot *vs* the distance to the oxigen atom. Arrows point out the equilibrium distances. Curves *3* and *4* show the same induced charges but in the case when the oxigen atom is approached to the opposite facet.

chemical bonds possesses the internal dipole momentum directed along the hexagonal axis; this dipole momentum is created by the alternating planes of the oppositely charged ions; (b) the energy of the excitons generated with light excitation in quantum dots is spent to break the chemical bonds at the facets, mainly at the anion one.

The mechanism of the photodarkening process is as follows. As the calculations show, Se-O and Cd-O bonding energies are decreased respectively to 50 kcal/mol and 30 kcal/mol in the excited state. This excited state is simulated by substituting one of the bonding state in the cluster wave function to an unbonding state. In a real structure, both the electron and hole can tunnel outside of a quantum dot into a glass matrix. Thus, the nonequilibrium electron from the electron-hole pair created by light can be trapped at the E^{-1} center in a matrix, if the temperature is sufficiently low [14], or it can be trapped by a surface trap. The nonequilibrium hole can also be trapped at H_1 centers in a matrix [14] or it can move to the negatively charged anion facet of a quantum dot, which is equivalent to the break of Se-O chemical bond. *Ab initio* calculations show that the break of Se-O bond increases the negative potential at the anion facet and the difference of the potentials between the cation and anion facets in a quantum dot. The electric field created

in a quantum dot induces the diffusion of single charged cadmium vacancies to the surface. As a result, acceptor centers inside a quantum dot disappear, while corresponding photoluminescence bands vanish. Note, when the vacancy leaves the quantum dot, its crystal structure is ordered, whereas the number of the dangling bonds at the dot surface is increased. This mechanism is confirmed by the photoinduced character of the photodarkening process. It also goes effectively at 4.2 K temperature, even if the light intensity is not sufficient to heat a quantum dot [15]. To restore the photoluminescence signal after phododarkening, it is sufficient to heat the structure up to 300–500 °C. At the annealing temperature new point defects (cadmium vacancies among them) are formed.

The validity of this mechanism can be confirmed by the experimental testing the conclusions stemming from it. In particular, the increase of a number of dangling bonds at the quantum dot surface is confirmed by the increase of the refraction index in these structures [8], as well as by both the reduction of the Kerr susceptibility and carrier lifetime [3]. The photoinduced absorption near the fundamental band edge is also attributed to the dangling bonds [8]. The photoinduced annealing of the acceptor states and the possibility of their reproduction by means of the temperature annealing are clearly confirmed by the degradation and recovery of the acceptor photoluminescence bands. The reduction of $\bar{\tau}$ with decrease of the dot average radius is simply explained by more fast departure of the cadmium vacancies to the surface in a small quantum dot.

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