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Formation and Growth of Semiconductor Nanocrystals in Phosphate Glass Matrix

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Abstract

Phase decomposition of the oversaturated solid solution of semiconductors in glass and the evolution of the ensembles of nanocrystals formed in the media are studied with optical absorption spectroscopy and modeled theoretically. Observed in the experiments difference of temporal behavior of the mean size of the nanocrystals for different levels of the oversaturation coincides with the results of numerical calculations within the frames of the model developed. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Glassy media embedded with semiconductor nanocrystals are of interest both for fundamental studies of quantum confinement phenomena and for applications in optoelectronics and nonlinear optics. The nanocrystals are conventionally being formed via the phase decomposition of semiconductors in the glass matrix. Existing models of the evolution of the oversaturated, solutions describe satisfactory the latest stage of the decomposition that is coalescence.[1–3] For this stage time dependence of the mean radius of the nanocrystals is close to $r \sim t^{1/3}$. However the, experimental studies of the nanocrystals' size growth show that the beginning growth dependence can he different.[4,5] Here we present results of optical studies of the evolution of the ensemble of CdSe nanocrystals formed in phosphate glass, and compare the behavior of the ensemble with developed theoretical model and numerical calculations.

2 Experimental

We used P_2O_5–Na_2O–ZnO–AlF_3–Ga_2O_3 glass system doped with CdSe. Phosphate glass system was chosen for the experiments as the system is more flexible comparatively with conventional silicate glass system, and it allows increasing concentration of semiconductors in glasses comparatively to silicate glasses.[6] Measured concentration of CdSe was ~1 wt%. Annealing of the glass samples at 400–460°C leads to their coloring from light yellow to dark red, the coloring depends on the annealing conditions. This behavior is similar to the behavior of conventional silicate glasses, where phase decomposition of the oversaturated solid solution occurs[4] and it is also induced by quantum confinement phenomena in CdSe semiconductor nanocrystals embedded in the glass matrix.[4,7] Electron microscopy and X-ray diffractometry studies of the annealed phosphate glass samples also showed existence of the nanocrystals. The temperature of the processing of the designed phosphate glass was not so high as necessary annealing temperature of conventional silicate glasses (620–660°C) as well as the annealing procedure was shorter: several minutes and tens of minutes instead of several hours and tens of hours for silicate glasses.

The quantum confinement of charge carriers within the nanocrystals influences the optical absorption spectra of the nanocrystals. The quantum confinement leads to the formation of distinct optical transitions, the mean radius of the nanocrystals can be deduced from the position of the first peak of absorption spectrum, that is the energy of the first optical transition.[4,7] The closer the peak to the absorption edge of the bulk semiconductor, the bigger the radius. Evolution of the

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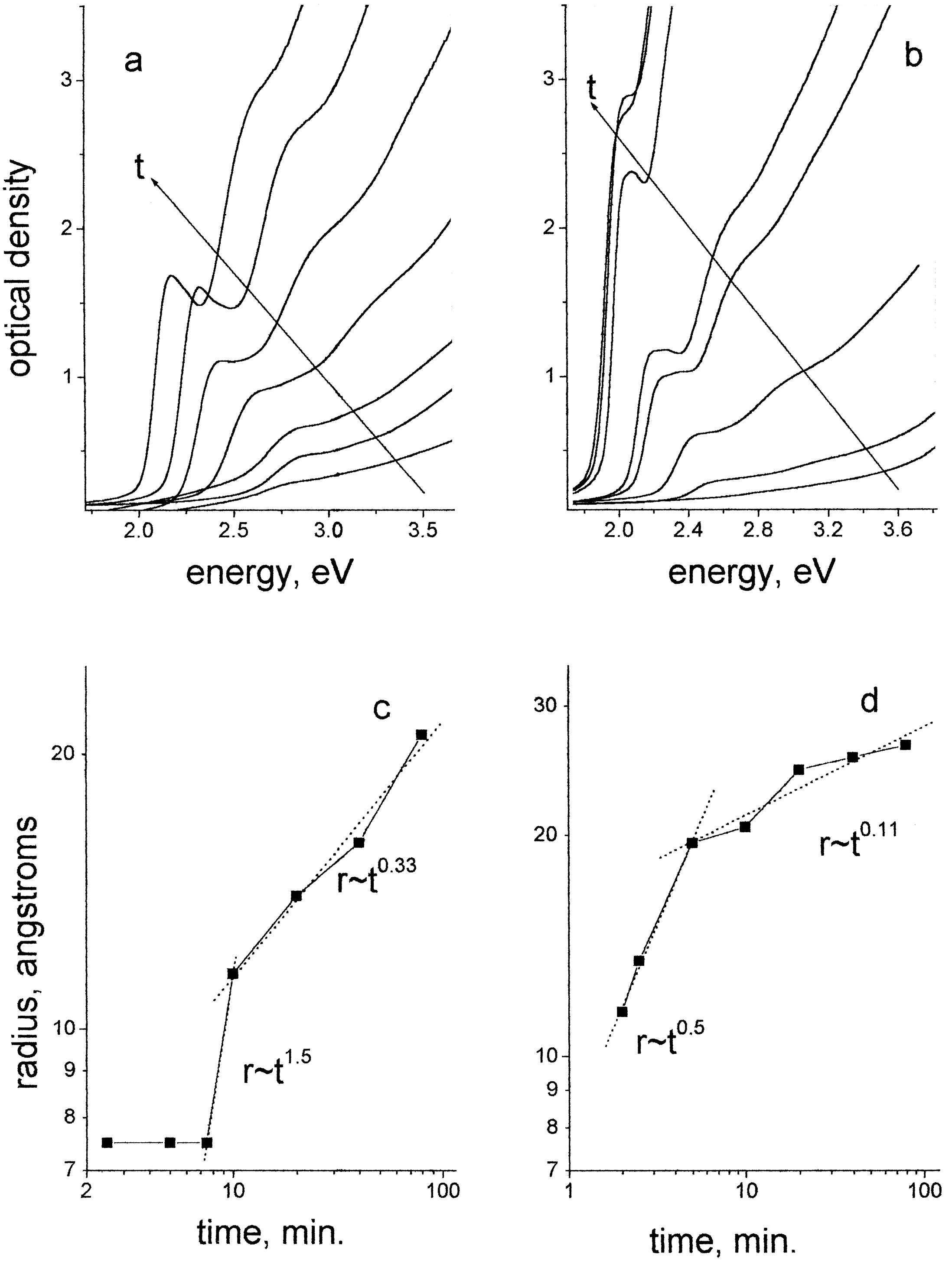

Fig. 1. Observed evolution of optical absorption spectra (a, b) and deduced from the spectra mean radius (c, d) of CdSe nanocrystals grown in the same phosphate glass under annealing at (a, c) 452°C and (b, d) 460°C. Plots (c) and (d) are in double logarithmic scale.

optical absorption spectra observed under annealing of CdSe-doped phosphate glass samples at two different temperatures is illustrated with Fig. 1(a) and (b), and the temporal dependence of the mean radii for these temperatures is presented in Fig. 1(c) and (d). The mean radii are deduced from the optical absorption data. It is necessary to point out that annealing of the same glass at higher temperature changes parameters of the solid solution: oversaturation drops due to increasing of the solubility, and diffusion coefficient increases. Plot Fig. 1(c) corresponds to lower temperature and higher oversaturation. It demonstrates fast growth of the mean radius at $t \sim 7{\cdot}5$ min, and double log scale makes evident $r \sim t^{1/3}$ growth for longer annealing. Figure 1(d) demonstrates two different slopes of $\ln(r) = f(\ln)(t))$ dependence. None of these slopes corresponds to coalescent growth.

3 Model

Formation and growth of the nanocrystals in the oversaturated solid solution can be described by kinetic equation with one stop jump (one particle absorption and desorption):[1]

$$\frac{\partial f}{\partial t} = p_{n-1}^{+} f_{n-1} - \left(p_n^{+} + p_n^{-}\right) f_n + p_{n+1}^{-} f_{n+1}$$

where f = distribution function of the nanocrystals by number of cells n; p^+ and p^- = probabilities of absorption (+) and desorption (–). Kinetic equation satisfies condition of mass conservation:

$$\frac{\mathrm{d}}{\mathrm{d}t} \sum_{n=1}^{\infty} n \cdot f_n = 0$$

Oversaturated solution, even if it contains nanocrystals, is a metastable media—smaller nanocrystals dissolve, but the bigger ones are stable, and they grow. Bound for these cases is R_c—critical radius. Nanocrystals of radius R_c do not dissolve and do not grow.

These nanocrystals are called the critical ones. Probability of the formation of the critical nanocrystal is $\sim \exp(-F_c/k_B T)$, where F_c = the free energy of the critical nanocrystal, T = the temperature in K, k_B = Boltzman constant. For critical nanocrystal p^+ is equal to p^-.

Probabilities of the one step jump for a nanocrystal were described by Wagner:[2]

$$p^{+} = kS\left(C_{\infty} + (C_0 - C_{\infty}) \frac{1 + kR_c/D}{1 + kR/D}\right);$$

$$p^{-} = kS\left(C_{\infty} + (C_0 - C_{\infty}) \frac{R_c}{R}\right)$$

Here S = the surface area of the nanocrystal, C_0 = the concentration of CdSe in the solution, C_∞ = the concentration of CdSe in the saturated solutions R = the radius of nanocrystal, k and D = the kinetic and diffusion coefficients.

The system of kinetic differential equations describes formation and growth of the nanocrystals in solid solution. The influence of the size distribution of the nanocrystals on the absorption of material was described by Efros.[7] Optical absorption of a nanocrystal is proportional to its volume. We can write the distribution function of optical density as

$$g = \frac{4\pi R^3}{3} \frac{\partial f}{\partial R}$$

The analysis of the position of the first optical absorption peak (1st optical transition) in spectra of optical absorption allows us to deduce mean radius of the nanocrystals. This radius corresponds to the maximum of the distribution function g.

4 Numerical Solution

The kinetic equation with this transition probability was numerically solved by Euler technique using variable step. Varying time step allows getting pinpoint accuracy. The simulation has shown that temporal behavior of the distribution function for the beginning growth stages differs for low and high levels of the initial oversaturation.

4.1 High oversaturation ('strong' nonequlibrity)

High oversaturation means that the solid solution is non-stable even for small fluctuations, or, the same, free energy of critical nanocrystals is low. Probability of forming the critical nanocrystal is high, and overcritical nanocrystals are generated.

First stage of the phase decomposition of the oversaturated solid solution under annealing gives rise to some quantity of overcritical nanocrystals. Saturation of the solution decreases, and critical radius increases. Computed transformation of the function g is illustrated with Fig. 2(a), (t_i, t_2, ..., t_5). The plot of the $g(R)$ maximum's radius for this case demonstrates jump—see Fig. 2(b). The jump occurs when integrated impact of the second lobe ($R \propto R_c$) of the function $g(R)$ dominates over impact of the first lobe ($R \gtrsim 0$). This corresponds to t_4 in the used time scale. When critical radius reaches the maximum's radius of the second lobe, lesser of them dissolve, and coalescence by Lifshits–Slesov[3] begins. Further phase decomposition corresponds to the classic coalescence law and dependence $R \sim t^{1/3}$ can be observed for the mean radius.

4.2 Low oversaturation ('weak' nonequlibrity)

When initial oversaturation is low (this can be provided by increasing temperature of the same solid solution; the increase of the temperature leads to the increase of the solubility and decrease of the oversaturation), the behavior of the distribution function changes.

Low oversaturation and big critical radius correspond to high free energy of the critical nanocrystals, and fluctuative creation of critical nanocrystals is practically eliminated. The phase decomposition of the solid solution under annealing

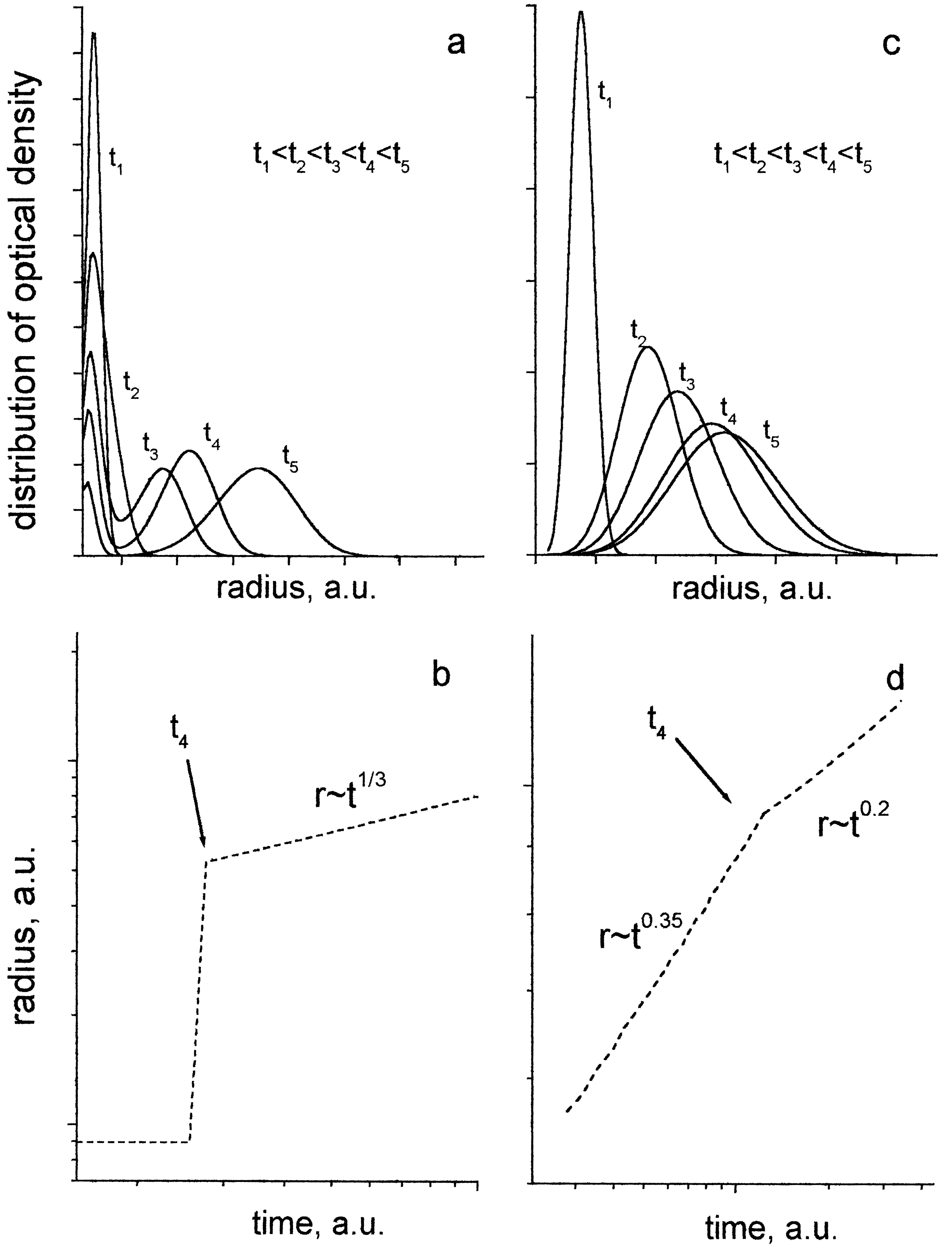

Fig. 2. Modeled evolution of the distribution function of optical density $g(R)$ (a, c) and temporal dependence of the $g(R)$ maximum's radius for the cases of (a, b) higher and (c, d) lower oversaturation of the solid solution. Plots (b) and (d) are in double logarithmic scale.

leads to the relaxation of the subsystem of the nanocrystals with sizes lower than the critical one—see Fig. 2(c) (t_1, t_2, ..., t_5). This relaxation reflects in the function $g(R)$ as growth of the maximum's radius. This case corresponds to $t < t_4$ in Fig. 2(c). When distribution of the nanocrystals becomes quasi-equilibrium ($t \sim t_4$), the functions $f(R)$ and $g(R)$ are practically unchangeable.

However this stage is not equilibrium—subsystem of bigger nanocrystals is not stable. These nanocrystals are still slowly growing, and oversaturation is slowly decreasing. The same dependence can be seen in the growth of the $g(R)$ maximum's radius—see Fig. 2(d), $t > t_4$. Power of dependence $R(t)$ can vary: $R \sim t^{0.3-0.5}$ for relaxation to quasi-equilibrium stage ($t < t_4$), and $R \sim t^{0.1-0.2}$ for the relaxation of the quasi-equilibrium system of nanocrystals ($t > t_4$). Similar character of growth was also observed experimentally—see Fig. 1(d).

5 Conclusion

Comparison of the experimental data with the results of the modeling demonstrates qualitative coincidence of the experimental and theoretical temporal dependence of the mean radius of the nanocrystals growing in the glass under annealing at the beginning growth stage. The temporal behavior of the nanocrystals' size is different for high and low oversaturation of the solid solution, and it can vary with the level of the oversaturation.

Acknowledgements

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