

Optical transmission spectra of a silicate glass containing nanocrystallites of cadmium sulphoselenide

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Abstract. The optical transmission spectra of $\text{CdSe}_x\text{S}_{1-x}$ doped low viscosity silicate glass are experimentally studied. Glass samples were subjected to one- or multi-step heat treatment for different lengths of time. We have followed the modification of the absorption spectra after each heat treatment. The red shift of the absorption edge and the accompanying change of coloration from orange to red are explained by size-quantization effects in the energy spectrum of electrons and holes in semiconductor nanoparticles thermally developed in low viscosity glass matrix. X-ray diffraction data show no stoichiometry changes during the heat treatment processes. Crystallites composition ($x \approx 0.5$) defined from the diffraction peaks was very close to the value estimated from the position of absorption edge.

PACS. 79.60.Jv Interfaces; heterostructures; nanostructures – 78.20.Ci Optical constants (including refractive index, complex dielectric constant, absorption, reflection and transmission coefficients, emissivity) – 78.40.Fy Semiconductors

1 Introduction

In recent years the optical and electrical properties of composite materials (CM) with semiconductor inclusions embedded in a dielectric matrix have been widely investigated [1]. It is well known that due to nanometric sizes of semiconductor inclusions, new effects connected with size quantization of the energy spectrum of electrons and holes can be observed [2–4]. The detailed experimental study of CM has shown that the fabrication and the processes of consequent heat treatment have an essential influence on the optical properties of a CM [5, 6].

A number of works have been devoted to the optical properties of CM containing elementary or binary semiconductors [1]. However the optical properties of CM with nanoparticles of semiconductor solid-solutions have not been studied in detail, although silicate glasses doped by ternary semiconductor alloy $\text{CdSe}_x\text{S}_{1-x}$ were widely used for the fabrication of signal red glasses (selenium ruby glass [7]), and nonlinear optical elements [8, 9]. A narrow nanocrystal size distribution is always necessary for many applications of such materials.

It is known that the size distribution of crystallites is determined not only by the kinetics of nucleation and growth of particles, but also by the glass viscosity and diffusion velocity of the solvent ions in the glass matrix. One

can expect that the lower the viscosity of the glass the narrower will be the size distribution of thermally developed crystallites in the glass matrix.

It is the purpose of the present paper to fabricate $\text{CdSe}_x\text{S}_{1-x}$ doped low viscosity silicate glass and to study the mechanism of changing of their optical transmission spectra as a consequence of the heat treatment. For this purpose the content of the glass network modifier component, in our case Na_2O , in the initial batch was taken about 20%, which is three times higher than in conventional glass [11].

2 Sample details and experimental outcomes

Samples of silicate glass containing $\text{CdSe}_x\text{S}_{1-x}$ semiconductor nanocrystals were prepared using the standard glass technology. The total amount of semiconductor constituents (CdS and CdSe) in the initial batch was about one percent in weight. The selenium-to-sulphur mole fraction in the initial batch was equal 0.625, which, as follows from the results of Borrelli *et al.* [11], ensures to obtain the $\text{CdSe}_x\text{S}_{1-x}$ alloy composition in crystallites near $x \approx 0.5$. The melting process was carried out at temperatures of 1350–1400 °C. During the fast cooling of the melt a supersaturated solid solution of a semiconductor and silicate glass is formed, which as a rule is a colorless. At room temperature such metastable phase can exist for an arbitrary

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long time. However during the heat treatment the disintegration process starts resulting in fluctuational formation of semiconductor nucleus and their growth in sizes due to progressive diffusion of ions Cd, Se, S, initially dispersed in the glass matrix.

The investigated samples had a form of plane-parallel plate, polished on both sides and with a thickness up to one millimeter. Transmission spectra were measured in the spectral range 200–1000 nm.

Samples of $\text{CdSe}_x\text{S}_{1-x}$ embedded silicate glass after manufacturing were subjected to heat treatment in air at different temperatures. It has been checked that heat treatment at temperatures lower than 400 °C (even for very long annealing time) does not result in any noticeable modification of optical transmission spectra of the samples. At higher temperatures we observed a significant shift of an absorption cut-off towards longer wavelengths and as a rule such shift is accompanied by the modification of the sample's color to yellow and then to red.

3 Results and discussions

The transmission spectra of glass samples, measured at room temperature before (curve 1) and after (curve 2-6) the heat treatment at 450 °C, are shown in Figure 1. The application of a heat treatment leads to the progressive formation of same microcrystalline phase of cadmium sulphoselenide. This can be observed in Figure 1 with the progressive formation of an absorption edge, which becomes more and more resolved and red-shifted with the thermal treatment time. At fixed annealing temperature of heat treatment the red shift of the absorption edge increases with time, but after sufficiently long time it ceased to shift. To cause a further shift one has to increase the heat treatment temperature (second step). To clarify the role of a glass matrix in transformation of the spectra we have measured also the transmission spectra of pure silicate glass with the same chemical composition as the others studied, but without semiconductor constituents. It was observed that the long heat treatment removes the mechanical strengths in the samples and as a result the glass becomes practically transparent in the wide spectral region 350–750 nm. Therefore one may conclude that the shift of the absorption edge of doped glass can be attributed only to the formation and growth of $\text{CdSe}_x\text{S}_{1-x}$ semiconductor nanocrystals in the glass matrix.

Spectral dependence of the absorption coefficient $\alpha = \alpha(\hbar\omega)$ can be easily calculated using data for transmittance of the samples:

$$T = \frac{(1 - K)^2 \exp(-\alpha d)}{1 - K^2 \exp(-2\alpha d)}, \quad (1)$$

where d is a thickness of the sample and K is the light reflectance from the sample surface – air boundary. We have found in our experiments that the reflection in the spectral range from 400 up to 600 nm is very small ($K < 0.04$) and with high accuracy it can be ignored in (1).

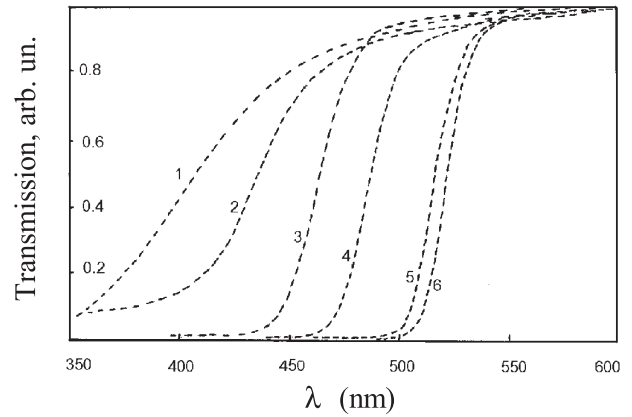


Fig. 1. Measured optical transmission spectra $T(\lambda)$ of $\text{CdSe}_x\text{S}_{1-x}$ doped silicate glass subjected to the heat treatment at 450 °C during different length of time. 1: 0 min; 2: 15 min; 3: 25 min; 4: 60 min; 5: 120 min; 6: 180 min.

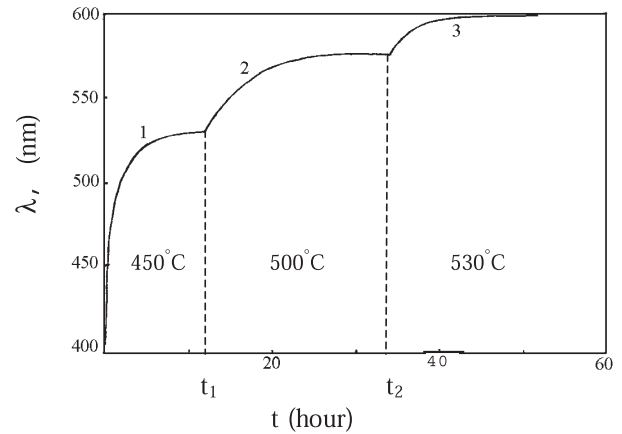


Fig. 2. Absorption cut-off $\lambda_{\text{cut-off}}$ shift during the heat treatment when the annealing temperature was raised at the moments t_1 and t_2 .

The spectral dependence of the absorption coefficient near the absorption edge (see Fig. 1) for the samples subjected to the sufficiently long isothermal annealing can be well fitted using the square root dependence $(\hbar\omega - E_g)^{1/2}$, which is known to correspond to the direct allowed transitions in semiconductors. Here E_g is the absorption edge, which corresponds to the effective band-gap of semiconductor crystallites.

Figure 2 shows the absorption cut-off as a function of heat treatment time carried out at three different annealing temperatures (450 °C, 500 °C, 530 °C). It is seen that for any given temperature the absorption edge approaches a certain limit after long heat treatment. But with increasing heat treatment temperature such dependence becomes weaker and disappears at temperatures higher than 550 °C.

We suggest that in our case the transformation of the optical absorption spectra in silicate glass doped with semiconductors CdS and CdSe is also governed by the presence of nanoparticles resulting from phase disintegration of supersaturated solid-solution.

Usually three stages of phase disintegration may be distinguished: nucleation process, diffusion growth of crystallites from supersaturated solution and coalescence, the last one being a diffusion-controlled competitive growth of large particles at the expense of the dissolution of the more small-sized [12, 13].

If the growth of crystallites after the nucleation is limited by diffusion supply from their direct surrounding and there is no interaction between them, then the average inclusion radius R should follow a square-root dependence on the growth time [13, 14]:

$$R(t) = R_0 + \sqrt{2Dt \frac{C_0 - C_e}{C_p - C_e}}. \quad (2)$$

Here C_0 and C_e are the initial and final concentrations of the semiconductor monomers in a matrix, C_p is the concentration of atoms in crystallite, D is the effective diffusion coefficient of semiconductor ions in glass matrix, R_0 is the average size at the starting time of the growth process.

The simplest model used to predict the optical properties of semiconductor doped glasses considers the effect of additional size-quantization of the electron and hole states in the spherical semiconductor crystallites with sizes in nanometer range. The strong quantum confinement results in a renormalization of the effective band-gap of semiconductor and consequently in the shift of the absorption edge with respect to its position in bulk semiconductor [15].

For the interband-absorption cut-off energy $\hbar\omega_0$ we can take the result of variational calculations, performed by Kayanuma [16] for the energy of lowest electron-hole state in spherical quantum dots, which is more appropriate to the $\text{CdSe}_x\text{S}_{1-x}$ doped glass since as we see later the crystallite size at higher heat treatment temperatures can be large and comparable to the exciton radius:

$$\hbar\omega_{off} = E_g + \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{1.786 e^2}{\varepsilon R} - 0.248 E_{ex}, \quad (3)$$

where $\mu = m_n m_p / (m_n + m_p)$ is the electron-hole reduced effective mass, R is the radius of the microcrystal, E_g , ε , E_{ex} are the bulk band-gap, dielectric constant and free exciton energy of $\text{CdSe}_x\text{S}_{1-x}$. For small particles (so-called strong confinement regime, $R \ll a_B$ where a_B is an exciton Bohr radius) the last two terms in (3) representing the Coulomb interaction effects can be neglected and the remaining part represents the energy shift, which results from independent quantization of the individual motions of electrons and holes. For large particles ($R \gg a_B$) the confinement terms in (3) can be omitted in the first approximation and one has exciton as in the bulk. Therefore, the band gap of bulk $\text{CdSe}_x\text{S}_{1-x}$ can be approximately taken to be equal to the absorption edge of samples subjected to the heat treatment at higher temperatures (for example, at 570 °C) for a very long time (several days). As it seen from Figure 2, the absorption edge approaches to the value $\lambda_{off} \approx 625$ nm, which corresponds to the

bulk material band-gap $E_g \approx 2$ eV and alloy composition $\text{CdSe}_{0.5}\text{S}_{0.5}$ [17].

This stoichiometry was conformed also by our X-ray diffraction measurements (not shown here). It is known that $\text{CdSe}_x\text{S}_{1-x}$ particles in the glass matrix crystallize in the hexagonal structure of wurtzite type [1]. Diffraction data show the presence of the peaks (110), (103) and (200) (in the angular range $40^\circ < 2\theta < 50^\circ$) and their positions are not changed by heat treatment time and temperature. The lattice constants of the crystallites have been found to be: $a = 4.16$ Å [1], $c = 6.76$ Å [5]. To find the alloy composition from the Vegard's law we must take into account that the $\text{CdSe}_x\text{S}_{1-x}$ nanocrystals embedded in a silicate glass usually suffer some compressive strain [18]. Therefore using for lattice constants of CdS and CdSe the values, defined by Borrelli *et al.* [11], $a(\text{CdS}) = 4.028$ Å, $c(\text{CdS}) = 6.547$ Å, $a(\text{CdSe}) = 4.225$ Å, $c(\text{CdSe}) = 6.866$ Å, we found $x \approx 0.5$, in good agreement with that obtained above from optical spectra.

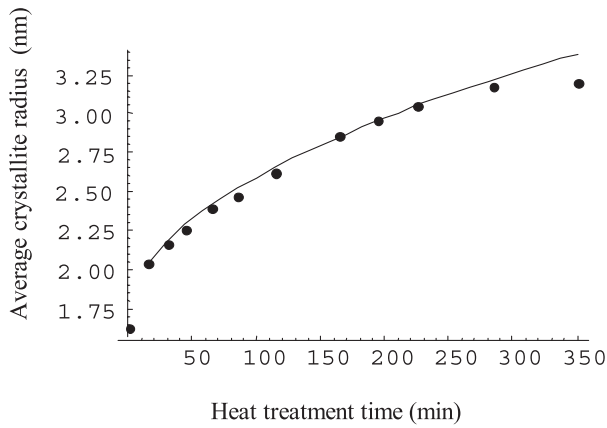
Using the measured data for $\hbar\omega_{off}(t)$ and equation (3) one can find the particle average radius for different heat treatment times (Figs. 3a, b). We use the following values for parameters $m_n/m_0 = 0.205$, $m_p/m_n = 1.020$, $\varepsilon = 8.46$, $a_B = 45$ Å, $E_{ex} = 30$ meV, appropriate to $\text{CdSe}_{0.5}\text{S}_{0.5}$ [17, 19]. During the initial period of heat treatment (process time less than 0.5 hour) we usually don't observe the characteristic for diffusion growth $t^{1/2}$ - dependence for particle radius R . Therefore in this case we are dealing with nucleation of semiconductor particles, only after which, the growth starts to be limited by the diffusion supply of semiconductor ions from glass matrix. Additionally this assumption is supported by the experimental observation, that the heat treatment at 550 °C results in a very fast (during several minutes) shift of the absorption edge from 380 nm up to 600 nm.

The time dependence of the average nanocrystals radius is described by the function (2) $R = R_0 + k\sqrt{t}$, where k depends on the diffusion coefficient. For example, for the annealing temperature of 450 °C this dependence can approximately be fitted to a form

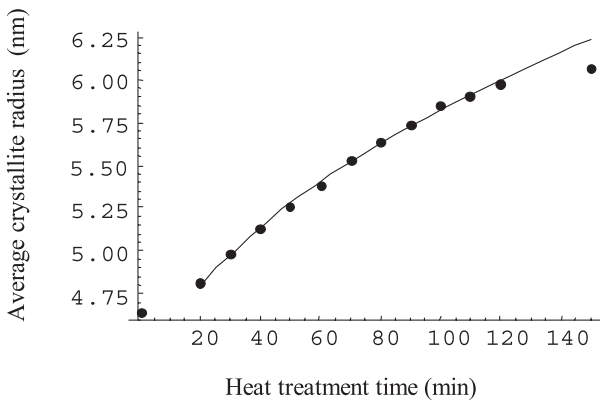
$$R(t) = \left(16 + 0.9\sqrt{t}\right), \text{ \AA} \quad (4)$$

where t is measured in minutes (see Figs. 3a, b). In other words after nucleation the semiconductor inclusions reach an initial average radius of 16 Å, then their diffusion growth starts. However, after the rather long time (usually more than 4 hours), a deviation from such dependence is seen (Fig. 3), which can be caused by depletion of matrix with solvent and very low level of supersaturation. According to estimates after the heat treatment at 450 °C for 4 hours hold time the size of crystallites reaches approximately 32 Å.

If the heat treatment is carried out at higher temperatures, for example at 500 °C, then diffusion growth of particles starts from the initial size of 32 Å. After saturation of the particle size at 450 °C, the further diffusion growth of particles can be done if the striking temperature is raised. In this stage an average radius of particles is



a)



b)

Fig. 3. Average radius of CdSe_xS_{1-x} nanoparticles as a function of heat treatment time for different annealing temperature $T = 450$ °C (a) and 530 °C (b).

increased from 32 Å up to 45 Å during 16.5 hours of heat treatment at 500 °C. The slower growth rate at 500 °C in comparison with the growth rate of particles at 450 °C, can be stipulated by a diminution of concentration of the semiconductor phases in a matrix.

For even higher striking temperature (more than 530 °C) the growth rate decays and particle radius starts to increase with time as $t^{1/3}$. Such dependence characterizes the process of particle coalescence described by the Lifshits-Slezov formula [20]:

$$R(t) = (4\sigma Dt/9)^{1/3}, \quad (5)$$

where σ is surface tension on interphase boundary.

To verify our model we explicitly investigated also the process of nucleation. As already remarked on a pioneering stage of heat treatment as a result of phase disintegration of super-saturated solid solution the fluctuation formation of semiconductor nucleus begins. It is known [21] that the critical size of nuclei R_0 depends on process temperature as

$$R_0(T) = \frac{2\sigma V_m T_0}{\Delta H(T_0 - T)}, \quad (6)$$

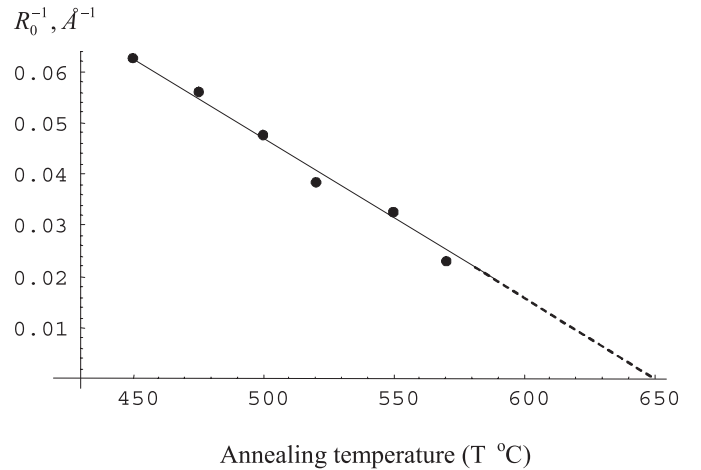


Fig. 4. Reverse mean critical radius of CdSe_xS_{1-x} nanoparticles as a function of annealing temperature.

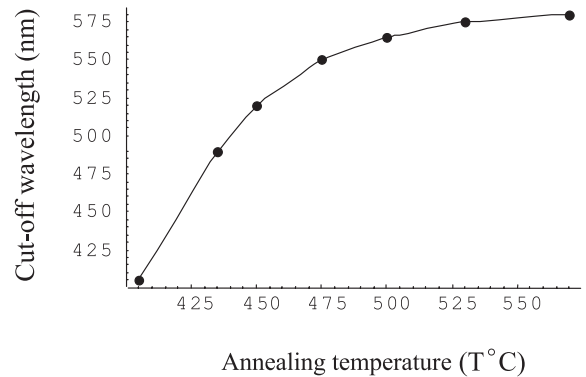


Fig. 5. Saturated absorption cut-off wavelength as a function of annealing temperature.

where V_m is the average specific volume of particles, ΔH is the average specific enthalpy, T_0 is the equilibrium temperature. From optical data the value R_0 has been determined for different heat treatment temperatures. As it is seen from Figure 4 a dependence (6) for $R_0^{-1}(T)$ can be well fitted with experimental data if the equilibrium temperature T_0 is taken equal to 650 °C.

As mentioned above for each striking temperature there exist a defined saturated edge of absorption. Figure 5 shows such an edge as a function of heat treatment temperature. In accordance with this the color of the samples is also changed. The higher the striking temperature the redder is the color. This effect can find practical application in devices for registration of temperature field with memory.

4 Conclusions

Using the standard glass technology, we have prepared samples of silicate glass-CdSe_xS_{1-x} ($x \approx 0.5$), which show strong dependence of optical transmission spectra on heat treatment regime. Due to low viscosity of glass matrix the rather large red-shift of the absorption edge (from 350 nm

to 600 nm) was observed for the relatively lower temperatures and shorter durations of the heat treatment. This shift is usually accompanied by the change of the glass color from orange to red. The experimentally observed shift of the absorption cut-off can be caused only by size-quantization of energy spectrum of electrons and holes in spherical nanoparticles of $\text{CdSe}_x\text{S}_{1-x}$ formed in a glass matrix during the disintegration processes of the initially supersaturated solid solution.

The analyses of the particle radii dependence on heat treatment temperatures and length of time confirm that such shift and saturation of absorption cut-off are governed by processes of nucleation of semiconductor nanoparticles, their diffusion growth in size and further possible coalescence. X-ray diffraction data show no change in crystallite composition during heat treatments, indicating that the change in glass coloration is mainly due to the increase in particle average size. The low viscosity of silicate glass matrix allows to obtain rather sharp absorption edges when doping with cadmium sulphoselenide. Such doped glasses could find applications as an optical filter in the spectral range 350–600 nm, as a signal red glass and also as a temperature field register.

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