Two different mechanisms of formation of quantum dots in borosilicate glass

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Abstract
The nucleation and growth of $Cd_{1-x}Zn_xS$ and CdS_xSe_{1-x} nanocrystals in
borosilicate glass are investigated through optical absorption and resonant
Raman scattering measurements. The optical absorption spectra are interpreted
with the help of a quantized-state effective-mass model applied for hetero-
geneous and homogeneous nucleation of nanocrystals. Stoichiometry changes
of the particles during the growth stage are monitored by resonant Raman
measurements. The findings indicate that the formation of $Cd_{1-x}Zn_xS$ particles
involves a stage of homogeneous nucleation and then a rapid transition to
ripening. No growth is observed. CdS_xSe_{1-x} particles undergo heterogeneous
nucleation and growth simultaneously with a gradual transition into the
ripening stage.

1. Introduction

Investigation of the electronic, optical, vibrational, and thermodynamical properties of nano-
metre-size semiconductor particles (quantum dots/nanocrystals) has been an important research
field for a decade [1–20]. Since the non-linearity of the properties of quantum dots is
significantly greater than that of the properties of bulk crystals of the same composition [2, 3],
quantum dots have an important potential device application as non-linear optical elements
[4]. Solid-phase precipitation of these structures in glass is one of the preparation routes
that has been used widely by researchers for many years [5, 6, 17–20]. However, the radii of
quantum dots exhibit a distribution about an average radius. The possibilities for technological
applications of quantum dots depend on the reduction of this size distribution. Growth regimes
of quantum dots in glass control the average particle size and size distribution. Therefore, for the
preparation of quantum dots in glass, it is important to determine how the type of initial particle
formation changes depending on the other parameters such as heat-treatment temperature and
time, composition of semiconductor used, and compound of the base glass.

Formation of quantum dots in glass occurs in three stages: (i) nucleation (either
homogeneous or heterogeneous), (ii) diffusion-limited growth, and (iii) coarsening (Oswald

ripening) [7–11]. Although there have been a number of studies of these stages, it is difficult to say under what conditions any one of these stages becomes important. When the optical absorption spectra for $Cd_{1-x}Zn_xS$- and CdS_xSe_{1-x}-doped borosilicate glasses are compared, a remarkable difference between the two is seen as regards the evolution of the spectra over time. This difference is explained by there being two different formation mechanisms at work. In this paper, the growth regimes for two different types of nanometre-size semiconductor particle are investigated with the help of (a) resonant Raman scattering measurements, to track the compositional changes, and (b) a quantized-state effective-mass model applied for heterogeneous and homogeneous nucleation, to explain the evolution of the absorption spectrum over time.

2. Experimental details and results

Samples were prepared from two unstruck (as-received) glass materials doped with Cd, S, and Zn (batch 1) and Cd, S, and Se (batch 2), supplied by Schott Glass Technologies. Small samples (~ 0.5 mm thick) were cut from these large samples. The two sets were heat treated at the same temperature: 625 °C for from fifteen minutes to three days. The amount of zinc incorporated into the particles (for the samples prepared from batch 1) and the S-to-Se ratio (for the samples prepared from batch 2) were determined by means of resonant Raman measurements. The results of the resonant Raman measurements have been published elsewhere for the batch 1 samples [7]. Raman spectra for three batch 2 samples are presented in figure 1. The spectra were excited with the 2.41 eV (514.5 nm) line of an argon-ion laser. The energy difference between CdS-like and CdSe-like modes varies nearly linearly with x as [14]

$$x = \frac{1.65(\Delta\omega - 60) + 5}{100} \tag{1}$$

where $\Delta\omega$ is the difference between the two modes in cm^{-1}. In figure 2, composition changes over time are presented. The composition of the $Cd_{1-x}Zn_xS$ particles changes remarkably with the heat-treatment time: the longer the heat treatment the greater the quantity of zinc incorporated into the particles (● in figure 2) [7, 13]. For CdS_xSe_{1-x} particles, the S content decreases to some extent with longer heat-treatment time (■ in figure 2).

The bulk band gaps of $Cd_{1-x}Zn_xS$ and CdS_xSe_{1-x} as functions of x are given by equations (2) and (3) respectively [15]:

$$E_g = 2.45 + 1.6x \tag{2}$$

$$E_g = 1.8 + 0.41x \tag{3}$$

where E_g and x are given in units of eV and as a percentage respectively.

It is important to track the composition of particles to ensure that the small blue-shift in the absorption spectra due to stoichiometry changes is subtracted from the blue-shift due to quantum confinement effects. The optical absorption spectra for $Cd_{1-x}Zn_xS$ and CdS_xSe_{1-x} particles embedded in glass and heat treated at 625 °C are shown in figure 3 and figure 4 respectively. The two sets were annealed at the same temperature in order to eliminate the effects which might arise due to temperature differences. In figure 3, an absorption peak forms between 3.1 and 3.3 eV with increasing heat-treatment time. During the formation of the peak, the absorption edges do not change much. In figure 4, absorption peaks between 2.5–2.7 eV and 2.8–3.0 eV form with increasing heat-treatment time. A well-structured spectrum evolves over time. As the peaks form, the absorption edges shift substantially to lower energies. In figure 3, the absorption edge for a bulk CdS sample and the absorption spectrum for a $Cd_{1-x}Zn_xS$-doped glass sample heat treated at 700 °C for 14 h are also shown for comparison.
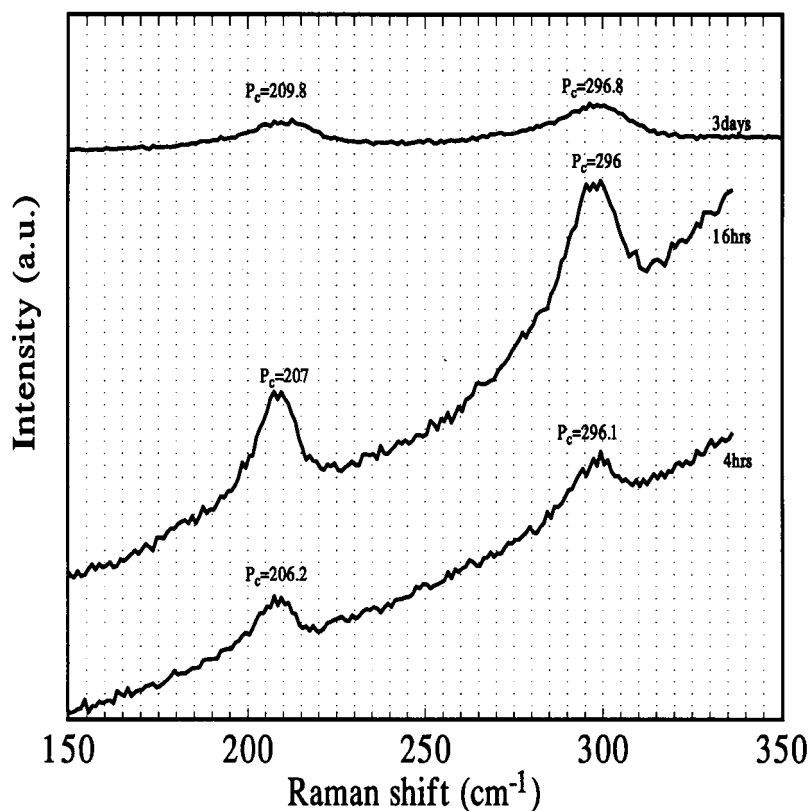
Figure 1. Raman spectra for CdS_xSe_{1-x} glass samples heat treated at 625 °C for 4 h, 16 h, and three days. P_c gives the position of the peak centre in cm^{-1}, determined by fitting the data to a broad quadratic background function and a single narrow Gaussian peak.
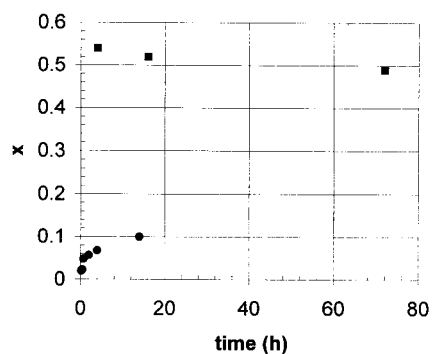

Figure 2. ●: the amount of zinc incorporated into $Cd_{1-x}Zn_xS$ particles over time. ■: the change of sulphur content for CdS_xSe_{1-x} particles over time.

The zinc content of the $Cd_{1-x}Zn_xS$ particles in this sample is $x \approx 0.2$, determined by means of resonant Raman scattering measurements. As the heat treatment continues, the particles grow over time. For large particles, quantum confinement effects are weak and the stoichiometry of the particle becomes important in determining the position of the absorption edge. Since
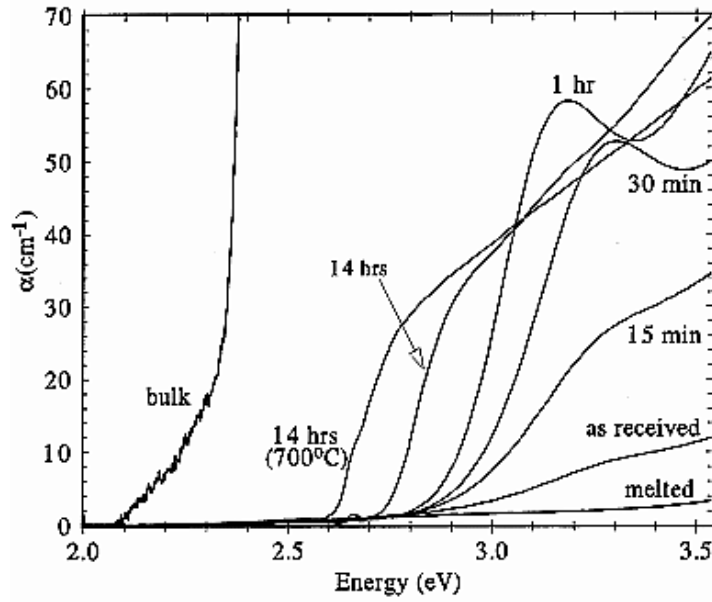
Figure 3. Optical absorption spectra for $Cd_{1-x}Zn_xS$-doped glass samples heat treated at 625 °C for various times, for a bulk CdS sample and for a $Cd_{1-x}Zn_xS$-doped glass sample heat treated for 14 h at 700 °C. The spectrum marked 'melted' is the absorption spectrum for the unstruck (as-received) glass sample melted at 1100 °C and quenched rapidly to room temperature.

the bulk band gap of $Cd_{1-x}Zn_xS$ is given by equation (2), for $x \approx 0.2$, $E_g \approx 2.77$ eV, which explains why the absorption edges of bulk CdS and $Cd_{1-x}Zn_xS$ with $x \approx 0.2$ do not coincide.

3. Modelling for heterogeneous and homogeneous nucleation

Employing Mie scattering and effective-medium theory to calculate the optical absorption due to quantum dots embedded in glass, the observed optical absorption coefficient at an energy of $h\nu = E$ for the composite (quantum dots/glass) can be expressed as

$$\alpha_{obs}(h\nu) = \sum_{R_{min}}^{R_{max}} \frac{(2l+1)}{\sigma\sqrt{\pi}} N(R) \exp\left\{ -\frac{[E-E(R)]^2}{2\sigma^2} \right\} \tag{4}$$

where $N(R)$ is a Gaussian weighting function for the particle size distribution, $(2l+1)$ is the oscillator strength of the transition, and σ is the standard deviation of the homogeneous broadening [12]. The $E(R)$ are the energies of the excited electron (e) and hole (h) states for a particle in a spherical box with a radius of R and are given by

$$E(R) = E_{bulk} + \frac{\hbar^2}{2R^2} \left[\frac{x^2_{n_e,l_e}}{m_e} + \frac{x^2_{n_h,l_h}}{m_h} \right] \tag{5}$$

where x_{n_e,l_e} and x_{n_h,l_h} are the roots of the spherical Bessel function. Details of the model calculation can be found elsewhere [7]. Numerical values from the literature were used. This model is applied below for homogeneous and heterogeneous nucleation of quantum dots. The first exciton peaks in the optical absorption spectra are used to characterize the formation of particles. It should be pointed out that the purpose of this application is to understand the
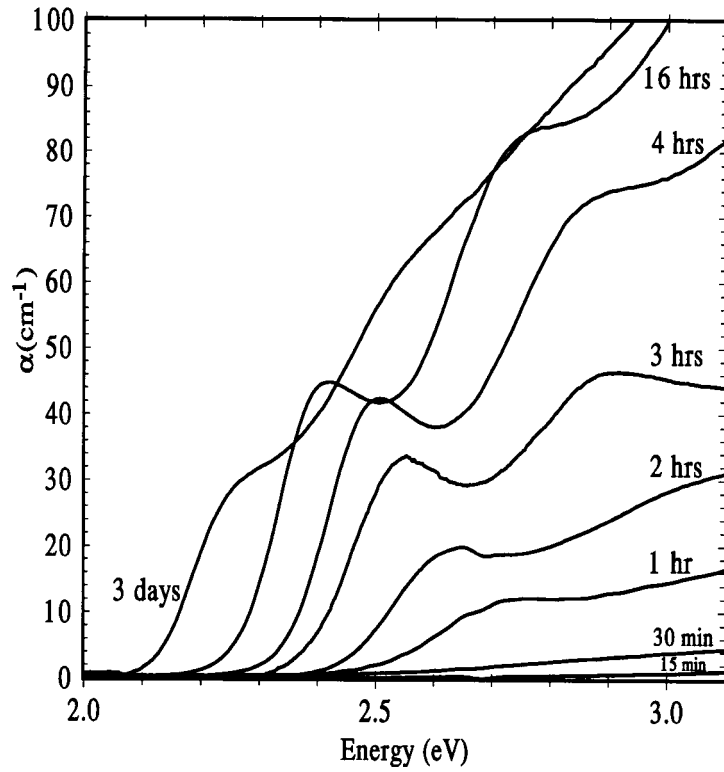
Figure 4. Optical absorption spectra for CdS_xSe_{1-x}-doped glass samples heat treated at 625 °C for from 15 min to three days.

evolution of the absorption spectrum over time for two different growth mechanisms, rather than to test the theory.

In homogeneous nucleation, particles are formed at $t = 0$ through nucleation by random fluctuations in the local concentration of reactants (Cd, Zn, S for $Cd_{1-x}Zn_xS$ quantum dots) [16]. The driving force for the fluctuation is the difference in Gibbs free energy (ΔG) of the final and initial states. If any fluctuation is able to lower the free energy, then the initial condition (α-phase: the clusters or precursors of a stable nucleus before forming the particle in glass) is unstable. In that case the only barrier to such fluctuation is the limiting atomic movement. Quantum dots are formed by heat treatment at $T \geqslant 550$ °C, which overcomes this barrier and the final stable state (β-phase: the clusters in the particle) is reached. The free energy of particle formation may be written as [21]

$$\Delta G = \frac{4}{3}\pi R^3 \, \Delta G_v + 4\pi R^2 \sigma \tag{6}$$

where $\Delta G_v = G_v^\beta - G_v^\alpha$, G_v^β is the Gibbs free energy of the β-phase (final phase), G_v^α is the Gibbs free energy of the α-phase (initial phase), and σ is the interface energy per unit area. The condition for thermodynamic equilibrium in a system in thermal and mechanical contact with the glass matrix (considered as a heat and pressure reservoir) is that the Gibbs free energy is a minimum. R_c is the critical radius of particles, which makes equation (6) minimum. Only those nuclei whose radius exceeds a critical value will grow. At the homogeneous nucleation stage, the average radius of particles $R(t) = R_c$, and does not change over time. The standard

deviation of the Gaussian particle size distribution during the homogeneous nucleation stage is given by

$$\Delta R = \left(\frac{3k_B T}{8\pi\sigma}\right)^{1/2} \tag{7}$$

where k_B is the Boltzmann constant. Inserting R_c into equation (4) and using equation (7), the absorption for the composite is calculated, and this is shown in figure 5 as a function of energy. In figure 5, it is observed that as more and more nuclei with the critical radius, R_c, are formed, the absorption increases but the absorption edge does not change.
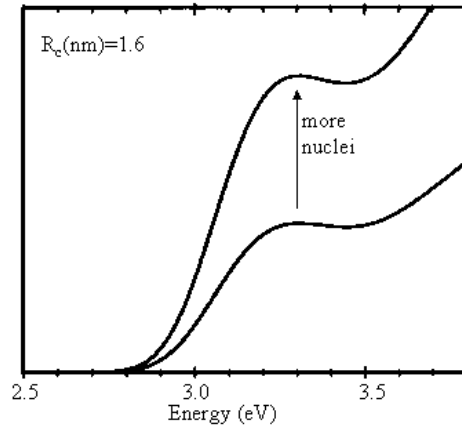

Figure 5. The absorption spectra calculated for a constant particle radius.

In the diffusion-limited growth where the particles grow by diffusion of the reactants (Cd, S, Se for $CdS_x Se_{1-x}$) to the surface of extrinsic nuclei whose formation is prompted during initial casting of the glass and before heat treatment, the average radius of the particles increases according to [22]

$$R(t) = R_0(1 + ct)^{1/2} \tag{8}$$

where R_0 is the initial radius, c is a constant, proportional to the normal growth coefficient, and t is the heat-treatment time. Inserting $R(t)$ into equation (4) above, absorption for the composite is calculated as a function of energy. In figure 6, the evolution of the calculated absorption spectra with heat-treatment time is shown. Here it is assumed that all nuclei are of the same size and formed at $t = 0$, and the standard deviation of the Gaussian particle size distribution is given by

$$\Delta R(t) = \frac{\Delta R_0}{(1 + ct)^{1/4}}. \tag{9}$$

In figure 6, it is observed that as the particles grow over time, the absorption edge shifts to lower energies and the magnitude of the relative absorption peak slightly increases.

4. Discussion

The optical absorption peak (first exciton peak) with $t \leqslant 16$ h for $CdS_x Se_{1-x}$-doped glass grows and shifts to lower energies simultaneously (see figure 4). The evolution of this peak is similar to that of the model absorption peak (see figure 6) calculated on the assumption
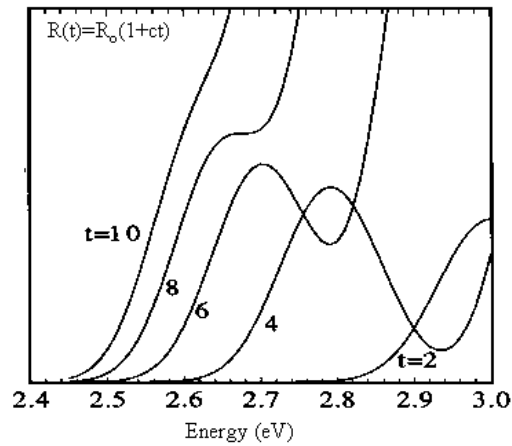
Figure 6. The absorption spectra calculated for various particle radii increasing over time.

that the particles grow by diffusion according to equation (8). Therefore, the shift to lower energies and rising of the peak indicate an increase in the size and number of the particles over time. This is an indication of heterogeneous nucleation for the growth of CdS_xSe_{1-x} particles in glass.

Neglecting R_0, equations (5) and (8) can be combined to yield

$$E_{peak} = E_{bulk} + \frac{A}{t}. \tag{10}$$

In figure 7, the optical absorption peak positions (in figures 3 and 4) are plotted against $1/t$; the magnitude of the peak increases. The slope of the least-squares fit to the data is $A = 0.33 \pm 0.05$ eV s for CdS_xSe_{1-x} and $A = 0.025 \pm 0.005$ eV s for $Cd_{1-x}Zn_xS$. This means that the rate at which the absorption peak position of the CdS_xSe_{1-x} particles moves to lower energies is 13 times more than that for $Cd_{1-x}Zn_xS$ particles. This is expected because
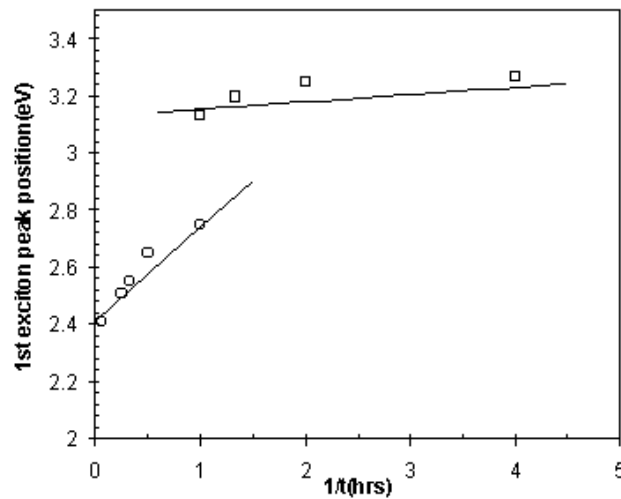

Figure 7. E_{peak} against $1/t$ for $Cd_{1-x}Zn_xS$-doped glass ($\square$) and for CdS_xSe_{1-x}-doped glass ($\bigcirc$).

heterogeneous (catalysed) nucleation requires much less Gibbs free energy than homogeneous nucleation. As the heat treatment continues, heterogeneously formed particles grow. This growth corresponds to a red-shift of the absorption spectrum over time, whereas, in figure 3, the way in which the optical absorption peak with $t \leqslant 1$ h, during which there is an increase in the magnitude of absorption, appears and grows resembles the case for the calculated absorption peak, which is produced by assuming homogeneous nucleation (see figure 5). Since no growth is assumed in producing the spectra in figure 5, the peak position does not shift over time. An increase in particle radius would cause an increase in both the peak position and the position of the onset of absorption, which is the case in the formation of CdS_xSe_{1-x} particles (as in figures 4 and 6). The shift observed in the peak position for $t \leqslant 1$ h in figure 3 cannot be ignored. However, that the rate of shift of the peak position over time in figure 3 is 13 times slower than that of figure 3 and that there is no shift in the onset of absorption while there is an increase in the magnitude of the absorption indicate that the dominant formation mechanism is homogeneous for $Cd_{1-x}Zn_xS$ particles in borosilicate glass. Particles with an average radius are formed and they do not grow. Details of the homogeneous nucleation of $Cd_{1-x}Zn_xS$ particles in silicate glass were reported elsewhere [23, 7]. Formation of $Cd_{1-x}Zn_xS$ particles in glass includes a homogeneous nucleation stage where particles with a critical radius (R_c) are formed over time. No growth stage is observed. Growth regimes of quantum dots control the size and size distribution of particles. On the other hand, the composition of the host material controls the number of particles. Higher particle-to-host volume fractions were recently obtained by preparing the nanocrystals in a novel phosphate glass [24]. The solubility of the reactants in the glass at the melting temperature sets an ultimate limit for the maximum number of particles. The volatility of sulphur and selenium at high temperature reduces the number of particles.

The effect of the base glass composition on both the formation mechanism and the size distribution of particles needs further research. It is possible that greater gains can be made by changing the glass composition in order to reduce the particle size distribution and increase the number of particles.

5. Summary

The formation of $Cd_{1-x}Zn_xS$ and CdS_xSe_{1-x} particles in borosilicate glass is studied by analysing optical absorption spectra with the help of a quantized-state effective-mass model applied for heterogeneous and homogeneous nucleation of particles. Resonant Raman scattering measurements were used to track the change in the composition of particles. The analysis indicates that the growth pattern for $Cd_{1-x}Zn_xS$ particles involves a stage of homogeneous nucleation and then a rapid transition to ripening. CdS_xSe_{1-x} particles appear to be undergoing nucleation and growth simultaneously with a gradual transition into the ripening stage.

Acknowledgments

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