Optical phonons and Raman scattering in ternary II–VI spheroidal nanocrystals embedded in a glass matrix

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Abstract

Theoretical and experimental studies of the spatial phonon confinement in ternary CdS x Se1–x nanocrystals embedded in a glass matrix formed by the composites (40)SiO2–(30)Na2CO3–(29)B2O3–(1)Al2O3 (mol%) + [[(2)CdO + (2)S + (2)Se] (wt%)] were carried out. From the analysis of the surface phonon modes, the theoretical procedure has allowed the determination of the geometrical characteristics of the nanocrystals. The calculated frequencies were compared with the experimental values obtained from the Raman spectra of CdS x Se1–x nanocrystals grown under different thermal treatments. A good correlation between the experimental and calculated CdS-like and CdSe-like surface optical modes was observed. The Raman selection rules and their connection with the nature of the surface optical phonons is discussed in order to use Raman spectroscopy as a probe to determine the composition x and the geometrical shape of the semiconductor nanocrystals.

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1. Introduction

The quantum confinement effects on the optical properties of nanocrystallites or quantum dots (QDs) grown over semiconductor-doped glasses are the subject of continuous and intense research. The main interest in these low dimensional materials arises because of their great potential of use in device applications due to their nonlinear optical properties. Experimental and theoretical studies showing the confinement effects on the electronic states and their energy levels are now quite well established. Nonetheless, the size effects on their phonon modes and on the electron–phonon interaction are still somewhat controversial. In this theoretical scenario, the answers to the question of how to determine the geometrical shape and its effects on the electronic structure and other physical properties in small QDs have not been sufficiently addressed. In II–VI QDs, the morphological effects can modify the energies, the symmetry properties of the wave functions and, thus, their allowed optical transitions.

In this paper, the connection between the phonon surface (SO) modes and the geometrical shape of a semiconductor QD are explored. By analyzing the behavior of the SO in ternary alloy based QDs, it has been shown that it is possible to determine the alloy composition x and the degree of deviation from the perfect spherical shape. To do this, the model developed by Comas et al. [1] for spheroidal QDs has been extended. For a ternary alloy A1−xBx, the...
dependence of the $A^1B$-like and $A^2B$-like SO-modes as a function of the concentration $x$ and the geometrical parameter $r$, that measures the degree of deviation from the sphericity, were calculated. The theory recovers the binary compound limits $x \to 0$ and $x \to 1$ of Ref. [1] by verifying the conditions $\omega_{\text{RTO}} < \omega_{\text{SO}} < \omega_{\text{LO}}$.

2. Experimental details

Samples were prepared on the glass matrix $\text{SiO}_2$–$\text{Na}_2\text{CO}_3$–$\text{B}_2\text{O}_3$–$\text{Al}_2\text{O}_3$ doped with $\text{CdO}$, $\text{S}$ and $\text{Se}$. The mixture was melted in an Aluminum crucible at 1200 °C, for 2 h. Then, it was quickly cooled down to room temperature. In order to enhance the diffusion of the $\text{Cd}^{2+}$, $\text{S}^{2-}$ and $\text{Se}^{2-}$ ions, a thermal treatment was performed at 600 °C using different annealing times of $t_a = 3, 5, 6, 10, 12, 14, 16, 18, 20, 22$ h, respectively. As a result of these thermal treatments, the QDs of $\text{CdS}, \text{Se}_1-x, \text{S}_x$ were formed on the glass matrix.

The QD Raman spectra were recorded at room temperature. An Argon-ion laser operating at 100 mW with the line $\lambda = 514$ nm was used for the Raman scattering. The scattered light was collected in the back-scattering geometry, using a Jobin–Yvon triple spectrometer.

Moreover, optical absorption measurements were carried out in order to determine the mean radius of the nanocrystallites. Finally, atomic force microscopy (AFM) characterization was performed in a subset of the samples in order to verify the validity of the main assumptions and results.

3. Theoretical model

Owing to the size decrease of a QD, its surface-to-volume ratio contribution to the Raman spectrum is much higher than that of bulk crystals. Therefore, in spheroidal nanocrystals surrounded by a glass matrix with a real frequency-independent dielectric constant $\varepsilon_D$, Raman observation of the SO-phonon modes with frequencies between the corresponding longitudinal (LO) and transverse (TO) bulk phonons modes might be expected.

The main macroscopic quantities involved in the description of the polar-optical phonons are derived from the equation $\varepsilon(\omega) \nabla^2 \varphi = 0$, where $\varphi$ is the electrostatic phonon potential and the frequency-dependent dielectric function for a ternary mixed crystal is given by [2]

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{X_1}{\omega_1^2 - \omega^2} + \frac{X_2}{\omega_2^2 - \omega^2}.$$  

Here, the subscript 1 (2) refers to the CdSe-like (CdS-like) mode. The polarizability parameters for the two TO-modes can be written as

$$X_1 = (1 - x)\varepsilon_1\varepsilon_\infty(\omega_{1,\text{B}}^2 - \omega_{1,\text{B}}^2),$$

$$X_2 = x\varepsilon_2\varepsilon_\infty(\omega_{2,\text{B}}^2 - \omega_{2,\text{B}}^2),$$

where the subscript B indicates that the phonon frequencies are those of the binary compound with high-frequency dielectric constants $\varepsilon_1\varepsilon_\infty$ and $\varepsilon_2\varepsilon_\infty$.

The LO-phonon modes are obtained from $\varepsilon(\omega) = 0$; thus Eq. (1) gives the LO frequencies of the CdS-like and CdSe-like modes as the roots of a quadratic polynomial in function of $\omega_{\text{LO}}(1,2)$. These frequencies are size-independent, since the dielectric function only contains information on the constituent materials.

For the SO phonons, $\varepsilon(\omega) \neq 0$ is used. Thus the solutions of the Laplace equation should satisfy the usual electrostatic boundary conditions between two different media. The main result of the formalism developed by Comas et al. [1] for spheroidal QDs can be summarized in the following equation:

$$\varepsilon(\omega) = \left(\frac{d}{d\xi} \ln Q_1^{t}\right) \left(\frac{d}{d\xi} \ln R_n^m\right)^{-1}.$$  

Note that this is the formal expression of the electrostatic boundary conditions for a prolate spheroidal QD whose geometrical coordinates are $\xi \geq 1, -1 \leq \eta \leq 1$ and $0 \leq \varphi \leq 2\pi$. The condition $\xi = \text{constant}$, defines an ellipsoid of revolution where the $z$-axis is pointing along the ellipsoid’s major axis. For $1 \leq \xi \leq \zeta_0$, there is a $\text{CdS}, \text{Se}_1-x$ QD with a dielectric constant $\varepsilon(\omega)$, in the interior of the spheroidal region. The exterior region $\xi \geq \zeta_0$ defines the glass matrix with dielectric constant $\varepsilon_D$. The functions $Q_1^{t}$ and $R_n^m$ in Eq. (3) are related to the solutions of the Laplace equation for the regions $\xi \geq \zeta_0$ and $\xi \leq \zeta_0$, respectively.

The vibrational quantum numbers are given by $l = 1, 2, 3, \ldots$ and $|m| \leq l$. (see Ref. [1] for further details). In addition, the limit $1/\zeta_0 \to 0$ represents the purely spherical situation given by $\varepsilon(\omega) = -\varepsilon_D(l + 1)/l$.

Note that the right side of Eq. (3) depends on the QD geometrical shape through the spatial parameter $\zeta_0$. The information about the nature of the constituent material is entirely contained in the dielectric functions.

The frequencies of the SO phonons are calculated, solving Eq. (3) including the dielectric function for a ternary compound defined in Eq. (1). With these procedures, the results of Ref. [1] have been extended to treat ternary compound QDs.

It is important to mention that for perfectly spherical QDs the SO frequencies are independent of the size or shape of the dot. For QDs displaying spheroidal geometry, the SO frequencies should present an appreciable variation with the size and with the change of the geometric shape. In both situations the SO-modes depend strongly on the concentration $x$.

4. Results

Several pieces of experimental evidence confirm a clear tendency of increasing QD size distribution when the heat treatment time is increased. For a general review of the growth processes see Ref. [3]. The optical absorption measurements carried out with the samples of this study (not showed here) also corroborate this statement. It is possible to determine the mean radius of QDs from the relation
between the ground-state electron-hole pair energy, \( \Delta E \) and the radius \( R \) of the QD. \( \Delta E \) can be determined from optical absorption measurements. From the analysis of the first allowed optical transition and by applying a simple spherical model, it can be established that \( \Delta E \) is proportional to \( 1/R^2 \) [3]. By this procedure the following results for the samples are obtained: \( R = 22 \text{ Å} \) for \( t_a = 5 \text{ h} \), \( R = 25 \text{ Å} \) for \( t_a = 10 \text{ h} \), \( R = 27 \text{ Å} \) for \( t_a = 14 \text{ h} \) and \( R = 29 \text{ Å} \) for \( t_a = 16 \text{ h} \). As expected, the mean QD radius increases progressively with increasing thermal treatment time.

The formation of the QDs in the glass matrix was also verified by AFM measurements. In Fig. 1) the AFM images for samples (a) \( t_a = 10 \text{ h} \) in panel (a) and for \( t_a = 16 \text{ h} \) in panel (b) are shown. Due to the size of the tip, the QD base length is systematically overestimated in AFM measurements, as the lateral resolution is smaller than the vertical. Nevertheless, it is possible to obtain information about the QD aspect ratio from the AFM pictures. The apparent QD heights obtained from the AFM images for \( t_a = 14 \text{ h} \) and \( t_a = 16 \text{ h} \) samples are about 2.5 and 2.9 nm, respectively, which is in good agreement with the values obtained by optical characterization. Moreover, from AFM analysis, the size dispersion in the samples is approximately 10%.

Fig. 2(a) shows the measured positions of the peaks corresponding to the LO CdS-like and CdSe-like modes as a function of the heat treatment time. Fig. 2(b) shows the Raman profile lines (solid lines) for CdSSe QD with a heat treatment time of 12 h. Two Gaussian fitting lines are also shown. The presence of the expected SO-modes is clearly revealed by the weaker asymmetric Raman band in the lower energy sides (second Gaussian) and by the small red-shift of the main peak energies. On the other hand, the presence of surface phonons, unambiguously, reveals the formation of QD’s in the glass matrix, as these modes only appear as consequence of the strong spatial confinement.

The difference \( \Delta \omega \) between the CdS- and CdSe-like frequency modes is also shown. Note that these modes do not present an appreciable dependence with the size of the QD’s. The small frequency variation corresponding to \( \pm 2 \text{ cm}^{-1} \) can be attributed to strain or small spatial confinement effects on the phonon modes [4,5].

The positions of the peaks corresponding to the SO-modes, as a function of the heat treatment times, are presented in Fig. 1(c). The group of data labeled as \( \Delta \omega \) represents the difference between the SO-CdS and SO-CdSe modes. It is noted that the SO-phonons present a visible dependence with the size of the QD’s and this fact strongly suggests that the geometrical shape of the nanocrystals is deviating from a purely spherical form.

Next, the experimental data were compared with the theoretical results, in order to determine the mean value of the concentration \( x \) and the degree of deviation from the pure spherical shape.

To estimate the LO and SO frequencies of the ternary CdS,Se\(_{1-x}\) nanocrystals, the frequency of the TO-modes of CdSe-like and CdS-like phonons, that depends nearly linear on concentration \( x \) as \( \omega_{\text{TO},1} = 168 + 17x \text{ cm}^{-1} \) and \( \omega_{\text{TO},2} = 266 - 28x \text{ cm}^{-1} \) were analyzed. The LO and TO frequencies for CdSe and CdS binary compounds were \( \omega_{\text{LO},1} = 210 \text{ cm}^{-1} \), \( \omega_{\text{LO},2} = 302 \text{ cm}^{-1} \), \( \omega_{\text{TO},1} = 168 \text{ cm}^{-1} \) and \( \omega_{\text{TO},2} = 238 \text{ cm}^{-1} \) [6]. The dielectric constants were \( \varepsilon_{\infty,1} = 6.1 \), \( \varepsilon_{\infty,12} = 5.32 \) while for the host material, \( \varepsilon_D = 2.25 \) [4] was used.

Fig. 3 shows the calculated frequencies for CdS-like and CdSe-like modes as function of the concentration \( x \). The solid-line labeled as \( \Delta \omega \) represents the difference between these modes. A simple quadratic polynomial fitting shows...
that the relation between $\Delta \omega$ and $x$, is given by $\Delta \omega = 57.64 + 98.6x - 40.31x^2$. For comparison purposes, the fitting obtained by Miyoshi et al. [6] from the Raman scattering data for several concentrations $x$ is also shown. By comparing the experimental data presented in Fig. 2(b) with the theoretical results of Fig. 3, the difference $\Delta \omega$ is obtained as approximately $89.0 \pm 2.0 \text{ cm}^{-1}$. This value corresponds to a concentration $x = 0.39 \pm 0.02$ of S in the ternary compound. Moreover, a large systematic error exists when using only one single mode to determine the composition, since strain and phonon confinement effects lead to a shift of both CdS-like and CdSe-like modes in the same direction. In contrast, the compositional change produces a shift of these modes in opposite directions. In order to reduce this systematic error, two modes were used to determine the concentration $x$. The same arguments can be applied to the SO-mode case to determine the geometric characteristics of the QDs.

The dependence on the spatial parameter $\xi_0$ for the CdS and CdSe SO frequencies of the QD’s with $x = 0.39$, is shown in Figs. 4(a) and (b). The modes with angular momentum numbers $l = 1, 2, 3$ are considered. The numbers over the lines indicate the corresponding azimuth quantum number $m$. The limit $\xi_0 \rightarrow 0$ corresponds to
the pure spherical case. Note the splitting of the SO frequencies according to the condition \( m \leq l \) as well as the strong dependence on the dimension of the QD through the spatial parameter \( \xi_0 \). Is interesting to recall that spherical modes are \((2l + 1)\)-degenerated and do not exhibit spatial variations.

Another important aspect is to determine which is the predominant phonon mode in the Raman response. For non-spherical QD’s, the Raman selection rules only allow SO phonons with \( m = 0 \) and \( l = \) even integer [1,8]. The odd mode \( l = 1 \) is not allowed; however, defects and/or impurities in the QD’s break the symmetry and relax this rule, thus inducing Raman scattering with the participation of \( l = 1 \) modes.

5. Discussion

In order to analyze the geometric properties of the QDs, attention will be restricted to the selection rule \( l = \) even, \( m = 0 \) only. Fig. 4 shows the dependence of \( \Delta \omega \) for CdS- and CdSe-SO frequencies with the spatial parameter \( \xi_0 \).

![Fig. 4](image)

Fig. 4. (a) The CdSe-SO frequencies as a function of \( n \) for \( l = 1, 2, 3 \) for all possible values of azimuth quantum number \( m \) in the prolate ellipsoid QD. (b) Same plot for CdS-SO modes. The calculations were performed for \( S \) concentration \( x = 0.39 \).

<table>
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<th>SO-mode ((l, m))</th>
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<th>( \xi_0 )</th>
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<td>3.6</td>
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</table>

Table 1

These values were calculated from a comparison between the experimental data plotted in Fig. 1(c) and the theoretical values shown in Fig. 4. The concentration \( x = 0.39 \) obtained from Fig. 2 is used in the calculations.

for the cases of: \( l = 2, m = 0 \) and for \( l = 4, m = 0 \) (see Fig. 5).

Theoretical results will be compared for the samples in Fig. 1(c). The following results were found for different heat treatment times: 16 h (\( \Delta \omega_{SO} = 83.56 \text{ cm}^{-1} \)), 14 h (\( \Delta \omega_{SO} = 83.20 \text{ cm}^{-1} \)) and 10 h (\( \Delta \omega_{SO} = 82.14 \text{ cm}^{-1} \)). The corresponding parameters \( \xi_0 \) and the ellipsoid’s semi-axis ratio \( r = \xi_0 (\xi_0^2 - 1)^{-1/2} \) are summarized in Table 1.

Some important points can be drawn from these results: (a) Note for the \( l = 2, 4 \) SO-modes that, when the deviation from the spherical shape increases, the difference between the SO frequencies diminishes. (b) These QD’s present strong deviations from the spherical shape; for instance, for \( l = 2, m = 0 \) a semi-axis aspect ratio in the interval: 1.14 \( \leq r \leq 2.08 \) is obtained. (c) Larger size QD’s (large heat treatment times) present shapes closer to spherical geometry.

The theoretical values obtained for the aspect ratio are in good agreement with those extracted from the AFM images. From Fig. 1, it can be observed that, for the \( t_a = 14 \text{ h} \) sample, the value for the parameter \( r \) is approximately 1.3 and for the \( t_a = 16 \text{ h} \) sample, \( r \) is approximately 1.07. These data confirm the results obtained from the Raman spectroscopy (see Table 1). Additionally, they show...
that the QD shape becomes closer to the spherical form as the heat treatment time increases.

The samples with $\Delta \omega \gtrless 84.5 \text{ cm}^{-1}$ have not been considered; this large energy difference would suggest that SO-modes $l=1$ are excited in the Raman process. Although these modes are forbidden by the Raman selection rules in non-spherical shapes, they can be excited by the presence of impurities or by defects created during the nucleation process.

In general, modes with $l > 2$ present small contribution to the Raman response. Anyhow, for the sake of completeness we have also considered them in the present analysis.

6. Conclusions

The ternary CdS$_{1-x}$Se$_x$ QDs were grown using the fusion technique on a glass matrix. The growth conditions are determined by two factors: the molar concentration $x$ and the heat treatment time. In the Raman spectra measurements, the presence of surface modes associated to CdS-like and CdSe-like phonon branches were observed. The frequencies of these modes are dependent on the concentration $x$ and on heat treatment time. The results suggest that the QDs are not perfectly spherical in their shape. Comparing the theoretical results with the experimental Raman spectra and AFM pictures the molar concentration was determined to be $x = 0.39$. In addition, the shapes of the QDs exhibit a very strong deviation from the spherical geometry with the aspect ration in the range of $1.14 \leq r \leq 2.08$ for the selected set of samples.

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