Optical vibrational modes in (Cd, Pb, Zn)S quantum dots embedded in Langmuir–Blodgett matrices

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Abstract

Structures with CdS, PbS, ZnS quantum dots (QDs) produced using the Langmuir–Blodgett technique were investigated by infrared (IR), Raman and ultra-violet–visible (UV–Vis) spectroscopies. The QDs size derived from the analysis of UV–Vis spectra and high-resolution transmission electron microscopy images amounts to 2–6 nm. The IR and Raman spectra reveal longitudinal optical phonons localised in QDs and surface vibrational modes. The frequency positions of the surface optical vibrational modes are adequately described taking into account confinement of fundamental optical phonons in the QDs.

Keywords: Clusters; Fourier transform infrared spectroscopy; Quantum effects; Raman scattering

1. Introduction

In the last decade semiconductor low-dimensional structures such as quantum wells, quantum wires and quantum dots (QDs) cause growing interest due to their unique optical and electronic properties [1,2]. While optical properties of bulk crystals and thin films are fairly well investigated and understood, the study of optical properties of low-dimensional structures still requires significant theoretical and experimental efforts. A number of techniques such as self-assembling growth during molecular beam epitaxy [3], formation of QDs in solutions [4], in glass [5], through colloidal chemistry [6] is used for QD formation.

In this paper we present the results of investigation of vibrational spectra of CdS, ZnS, and PbS QDs formed in Langmuir–Blodgett (LB) matrices.

2. Experimental details

The standard LB technology allows to prepare the high quality films of Cd, Zn and Pb behenates. The behenates of these metals can react with the gaseous H₂S resulting in the formation of CdS, ZnS or PbS QDs [7,8]. In our experiments thin films of the behenates of Cd, Zn and Pb were deposited on the bare (001)-oriented Si substrates or the Si substrates covered by an Al layer of approximately 100 nm. The Al layer was used as a reference for measuring reflection infrared (IR) spectra. No difference of vibrational properties of the investigated LB films deposited on various substrates was observed. The thickness of LB films under investigation was 400 monolayers (1.2 μ). As prepared LB films were treated with H₂S at a pressure of 50–100 Torr for 3 h. As a result of the reaction

Me(C₂,H₄₃,COO)ₓ + H₂S = MeS + 2C₂,H₄₃COOH,

where Me = Cd, Zn, Pb, CdS, ZnS, PbS QDs were formed in a matrix of behenic acid.

IR reflection spectra were recorded at an angle of incidence (θ=75°) in ?-polarised light using the IR Fourier transform spectrometers Bruker IFS66 and IFS113v. The resolution was 2 cm⁻¹ over the whole spectral range and the number of scans was 500. An Al mirror was used as a reference sample. The LB films deposited on the (0 0 1)-oriented Si substrates were used...
for measuring IR transmission spectra at the normal incidence.

Raman scattering experiments were carried out using a spectrometer Dilor XY800 in backscattering geometry. Ar$^+$ and Kr$^+$ lasers were used as excitation sources in the range of wavelength of 514.5–457.9 nm (2.41–2.71 eV) with a power of 40 mW (power density of $10^{-2}$ W cm$^{-2}$). The spectral resolution was typically 3 cm$^{-1}$.

Ultra-violet–visible (UV–Vis) reflection/absorption spectra were recorded using a UV–Vis spectrometer Specord M-40 in the wavelength range of 250–800 nm with a spectral resolution of 10 cm$^{-1}$.

High-resolution transmission electron microscopy (HRTEM) experiments were performed using an electron microscope JEM-400EX (JEOL). The resolution over the HRTEM image was 0.165 nm. For these experiments, thin films (60 nm) with QDs were formed on a polymer film of a thickness of 100 nm deposited on a copper grating. Details of the experiment are reported in Ref. [9].

3. Results and discussion

The transformation of the behenates of Cd, Zn and Pb to behenic acid due to the reaction presented by Eq. (1) was confirmed through the IR transmission spectra of the LB films recorded before and after sulfidation (Fig. 1). The IR spectra before sulfidation reveal the minima in the spectral ranges of 1500–1550 and 1410–1420 cm$^{-1}$ assigned to the CO$_2^-$ asymmetrical and symmetrical stretching vibrations, respectively. After sulfidation these features disappear while a minimum at 1700 cm$^{-1}$ attributed to the C=O vibrations in the CO$_2H$ complexes occurs. This behaviour is found to be typical for sulfidation of the LB films [7,10]. An absorption line at 1466 cm$^{-1}$ attributed to the CH$_2$ scissors vibrations remains in all spectra because the CH$_2$ bonds do not take part in the chemical reaction.

The size of QDs was determined from the analysis of UV–Vis absorption spectra and further compared with the data obtained from HRTEM experiments. The absorption spectra of the samples with CdS, ZnS or PbS QDs shown in Fig. 2 reveal the features near 390, 270 and 255 nm attributed to the 1se–1sh interband transitions in QDs. Vertical lines in Fig. 2 indicate the position of band gap energies in bulk CdS and ZnS. The band gap of bulk PbS amounts to 0.4 eV and is not shown in the figure. We attributed the peaks near 400 and 300 nm in the spectra of the structures with PbS QDs to the 1se–1ph and 1pe–1ph transitions, respectively.

A simple model based on the effective mass approximation [11] allows the size of QDs to be determined via the energy of the 1se–1sh transitions as

$$E_{1se-1sh} = E_g + \frac{2h^2\pi^2}{D^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{3.56e^2}{\varepsilon D}$$

where $D$ is the QD diameter, $E_g$, $\varepsilon$, $m_e$ and $m_h$ are the band gap energy, dielectric constant, electron and hole effective masses in the bulk material composing the QD, respectively.

The dependence of the 1se–1sh transitions as a function of the QDs size calculated for CdS, ZnS or PbS QDs are shown in Fig. 3. The dashed areas indicate the energy of the 1se–1sh transitions determined from
UV–Vis spectra within the experimental accuracy. The size of ZnS, CdS and PbS QDs obtained from the comparison of experimental and calculated data amounts to (2.8 ± 0.2), (3.2 ± 0.1) and (4.2 ± 0.2) nm, respectively.

The QD size was also determined from the HRTEM images of the structures with PbS and CdS QDs shown in Fig. 4a and b, respectively. An average size determined from the figure is approximately (3 ± 1) nm for CdS and (4 ± 2) nm for PbS QDs which is in good agreement with the data obtained from the analysis of UV–Vis spectra. The distances between atomic planes of PbS and CdS QDs determined from HRTEM images refer to the cubic and wurtzite-type crystal modifications, respectively. The surface densities of PbS and CdS QDs are 2 \times 10^{12} and 10^{11} cm^{-2}, respectively.

Diffraction patterns from ZnS QDs were not obtained probably due to the small volume density of crystal particles ( < 1%), their small size and amorphous ZnS QDs smearing the diffraction picture. In addition, Zn is the lightest atom in comparison to Pb and Zn that makes difficult visualisation of the QDs.

Vibrational modes in the QD structures were investigated using IR and Raman spectroscopies. While transverse optical (TO) modes are not expected to be optically active, longitudinal optical (LO) modes can be observed in Raman and IR spectra [12].

Fig. 5 shows Raman spectra of structures with CdS, PbS and ZnS QDs embedded in a matrix of behenic acid. Vertical lines indicate the position of the TO and LO phonons in bulk CdS, PbS and ZnS. One can see that the frequency position of experimental Raman lines differs from those of optical phonons in the corresponding bulk materials. Confinement of optical phonons in QDs and/or Raman scattering by the surface optical phonons can be responsible for such behaviour. The size of QDs is appropriate to observe these effects [13]. The spectra of the structures with CdS and PbS QDs reveal
Raman peaks at 296 and 207 cm\(^{-1}\) which are attributed to LO phonon scattering in CdS and PbS QDs, respectively. One can see that the position of LO phonon in CdS QDs is lower than the bulk value of LO phonon (303 cm\(^{-1}\)) [14] while the frequency of LO phonon in PbS QDs exceeds the corresponding bulk value (205 cm\(^{-1}\)) [15]. The difference in phonon frequency positions in bulk materials and in QDs is explained by confinement of optical phonons [16]. The wave vector of confined phonons for the QDs of small size which can be approximated as a sphere is defined as \( q = \pi m / d \), where \( m \) is the quantum number of confined mode and \( d \) is the diameter of QDs. The dispersion \( \omega(q) \) of LO phonons in bulk CdS is negative hence the frequency position of the first confined mode (LO\(_0\)) observed in experiment (Fig. 5) is located below its bulk value. A shoulder near 250 cm\(^{-1}\) is due to the scattering by TO phonons in CdS QDs.

The dispersion of LO phonons in PbS crystals is not monotonic and positive in the range of wave vectors of \( q = 0 - 0.6 \pi / a_{\text{PbS}} \) \((a_{\text{PbS}} \text{ is the lattice parameter in PbS})\) [17]. Such dispersion causes an increase of the first confined LO\(_1\) phonon frequency position. Indeed, the value of LO\(_1\) confined modes observed in Raman spectra exceeds the frequency position of LO phonons in bulk PbS. The asymmetrical shape of the Raman phonon lines in the spectra can be due to the contribution of higher confined modes (with \( m > 1 \)).

The Raman line in the spectra of the structures with ZnS QDs is located at 320 cm\(^{-1}\) and cannot be interpreted as confined mode. This line is attributed to a surface vibrational mode in the QDs. The surface optical modes in spherical QDs embedded in a dielectric matrix should satisfy the following equation [18]

\[
\frac{\varepsilon_i(\omega)}{\varepsilon_m} = -1 - \frac{1}{l}
\]

where \( \varepsilon_i(\omega) \) is the dielectric function of the material composing the QD, \( \varepsilon_m \) is the dielectric function of the surrounding media and \( l \) is the quantum number of the surface optical mode. Calculation of the first surface mode in ZnS QDs in a matrix of behenic acid (\( \varepsilon_m = 2.4 \)) amounts to 320 cm\(^{-1}\) that corresponds well to the experimental value (316 cm\(^{-1}\)). No LO or TO confined optical phonons in the QDs were observed in the Raman spectra. Presumably, this is due to the small size of ZnS QDs for which a high surface/bulk ratio of atoms in QDs is realised. Indeed, in the small-size QDs, the number of atoms located at the surface becomes comparable or larger than those in the ‘bulk’ of QDs. This leads to an increasing contribution of the surface layers in Raman scattering process.

Fig. 6 presents the IR reflection–absorption spectra of the QD structures which exhibit broad features at the frequency range between the TO and LO phonon positions in corresponding bulk materials (indicated by vertical lines). These features are assigned to the first interface modes existing in QDs. The frequency position of the SO\(_1\) mode observed in the Raman spectra of the structures with ZnS QDs coincides with a minimum seen in the corresponding IR spectra. The calculations of frequency positions of the SO\(_1\) modes performed using Eq. (3) show a good correspondence with the experimental values derived from IR spectra. The reflection minimum observed in the spectrum of PbS QDs at 275 cm\(^{-1}\) exceeds the frequency position of the fundamental phonon frequencies and approaches the sum of the TO and LO phonon frequencies (67 + 205 cm\(^{-1}\)) in bulk PbS. Hence, this feature is due to two-phonon processes.

4. Conclusion

In conclusion, an optical investigation of structures with ZnS, CdS, and PbS QDs produced using the LB technique was performed. Optical phonons localised in QDs and surface optical modes were observed in the IR and Raman spectra. Surface optical modes were explained within dielectric continuum model of surface optical modes in spherical QDs. The size of QDs was determined using HRTEM, UV–Vis spectroscopy in combination with calculations.

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References


