Phonon Modes in Semiconductor Quantum Dots

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Phonon confinement effects are studied in self-assembled close-packed CdS and CdSe colloidal quantum dots using Raman scattering techniques. The longitudinal optical phonon frequency exhibits a red shift compared to the bulk mode in CdS quantum dot due to phonon confinement. High frequency phonon modes that are above the bulk LO phonon frequency are also observed in CdSe quantum dots. The possible origin of these high-frequency modes is attributed to the phonon density of states above the bulk LO frequency due to the surface states of the dots.

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I. INTRODUCTION

Semiconducting quantum dots are active materials in a large number of electronic and optoelectronic devices [1–6]. Colloidal quantum dots have drawn increasing interest due to their fascinating properties. The easy solution processibility helps to integrate them with a variety of substrates. Size-dependent tunable absorption and emission spectra, high absorption coefficients and large intrinsic permanent dipole moments are some promising features of the quantum dots, which separate them from bulk and other nanostructured materials. The three-dimensional confinement and zero-dimensional density of states in the quantum dots gives rise to a set of discrete electronic energy levels and discrete phonon modes. The optical phonons play an important role in the carrier relaxation processes in the quantum dots [7]. For example, the photoexcited electrons in the quantum dots may be able to relax to the ground state if the energy difference between the excited state and the ground state is very close to the energy of an optical phonon. By tailoring the size of the dots, this energy difference can be matched to that of an optical phonon. Such phonon-assisted transitions are widely used in quantum dot lasers [8–10]. Electron phonon interactions play a significant role in the transport processes in electronic and optoelectronic devices made of semiconducting quantum dots. At room temperature, the scattering rates of electrons with phonons affect the output of the devices to a large extent. These interactions are also relevant in determining the optical properties of semiconductor quantum dots. It has been observed that the interface phonons or the surface optical phonons (SO) in these quantum dots have an important role in the transport process in the quantum-cascade lasers and lead

to fast SO phonon-mediated depopulation in quantum-cascade terahertz emitters [11]. In view of these recent developments in the fields of quantum dot-based devices, it is important to study the different phonon modes in the quantum dots.

The dominant electron phonon coupling mechanism in the case of polar materials like CdSe and CdS is called the FrÖhlich interaction or polar interaction between the fields induced by the vibrational motion and the electronic charge density. The three-dimensional confinement in quantum dots leads to confined optical phonon modes and there are also SO phonon modes. Moreover, there is evidence that the surface reconstruction of the dots induced by different fabrication techniques leads to surface states and frequencies above the bulk longitudinal optical (LO) frequencies[12].

In this paper, we study the optical phonon modes in a self-assembled close-packed cadmium sulfide (CdS) sample and in a superlattice sample of cadmium selenide (CdSe) quantum dots using Raman scattering techniques at room temperature. We observe that the phonon confinement leads to a red shift in LO mode frequency in CdS quantum dots and blue shift in the CdSe quantum dots. A dielectric continuum model has been used to calculate the different LO and SO modes for CdS and CdSe dots and compared with experimental results.

II. FABRICATION AND EXPERIMENTS

A sample of self-assembled CdS quantum dots is fabricated by drop casting several layers of the quantum dots on a silicon substrate [13]. Further, a superlattice sample is fabricated with CdSe quantum dots by self-organization of close-packed quantum dots [14]. This sample is prepared on indium tin oxide-coated glass by slow evaporation of CdSe quantum dots from a solution of 90% octane and 10% 1-octanol by heating it at 80 $^{\circ}$C in vacuum for an hour. Raman scattering and photoluminescence (PL) measurements are performed on the two samples using an Acton SpectraPro 2500 and a helium-cadmium (He-Cd) laser or Ar^+ laser. Raman spectroscopy is performed in the backscattering geometry at room temperature with a macro-optic setup with an approximately 40^o angle of incidence on the sample. The incident light is suppressed by Raman notch filters in front of the spectrometer slit. A 2400-g/mm grating, which offers a resolution of 2.7 cm^{-1} with a laser excitation at 325 nm, is used.

III. RESULTS AND DISCUSSION

The PL spectrum from the CdS quantum dots is shown in Fig. 1. The sample is excited with a 325-nm laser line. The absorption measurements performed on these dots [13] and the PL in Fig. 1 indicate an approximate size of the dots of 3 nm.

The results of Raman scattering studies on this sample with a 488-nm line of Ar^+ laser are shown in Fig. 2. The LO phonon mode appears at 301.5 cm^{-1} and the 2LO mode appears at 603 cm^{-1} from these dots. The peak at 520 cm^{-1} is the standard peak

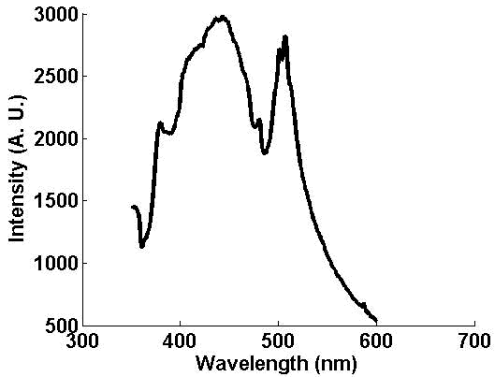

FIG. 1: PL from CdS quantum dot sample using a 325-nm laser excitation.

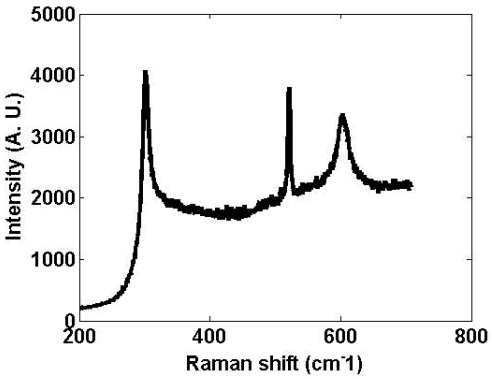

FIG. 2: Raman spectrum of the CdS quantum dots on silicon substrate at room temperature excited with a 448-nm laser. The LO peak is at 301.5 cm^{-1} and the 2LO peak is at 603 cm^{-1}.

from the silicon substrate. The frequency of the confined LO mode in these dots is shifted towards the red by $\sim$3 cm^{-1} compared to the bulk value of 304.5 cm^{-1} in CdS. This shift is consistent with a phonon confinement effect. The electron phonon coupling strength (S) can be estimated from the ratio of the intensities of the 2LO and LO modes [15]. The measured value obtained from the data is S $\sim$ 0.81.

The PL emission from the CdSe superlattice sample excited with a 442-nm line of He-Cd laser is depicted in Fig. 3. The emission peak is at about 650 nm. The PL reveals that there is a narrow size distribution of these dots, which peaks at approximately 7 nm. The poor passivation in these dots gives rise to low radiative recombination. This helps to observe strong Raman peaks from this sample.

Resonant Raman scattering is performed on this superlattice sample with a 325-nm line from He-Cd laser. Two strong peaks are observed at 237 and 390 cm^{-1}as depicted in Fig. 4. The bulk LO phonon frequency for CdSe is at 213 cm^{-1}. Thus, two high-frequency phonon modes that are above the bulk LO mode are observed. Similar features have been observed recently in CdSe nanoparticles (2-3 nm) in gelatin matrix by Dzhagan et al. [12]. High-frequency shoulders of the LO phonon peaks and their overtones have been observed. The participation of acoustic phonons in energy relaxation processes have been discussed as a possible origin of the high-frequency shoulder. It has also been attributed partly to the phonon density of states at the quantum dots surfaces above the bulk LO frequencies [16]. In the present study, the two strong peaks at 237 cm^{-1} and 390 cm^{-1} are observed without any broad shoulders. The first one is 14 cm^{-1}above the bulk LO frequency. A possible origin of these two peaks in the superlattice sample could be the surface states in the CdSe dots. The CdSe quantum dots in the superlattice are core-only dots with unpassivated surfaces. Surface reconstruction results in phonon frequencies higher than the bulk value. There is finite density of phonon states above the bulk LO mode due to the surface states [16]. A weak SO mode is also observed around 204 cm^{-1} at the shoulder of the peak at 237

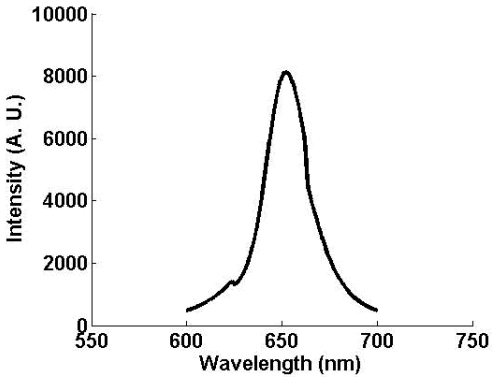

FIG. 3: PL results from the CdSe superlattice sample excited with a 442-nm laser.

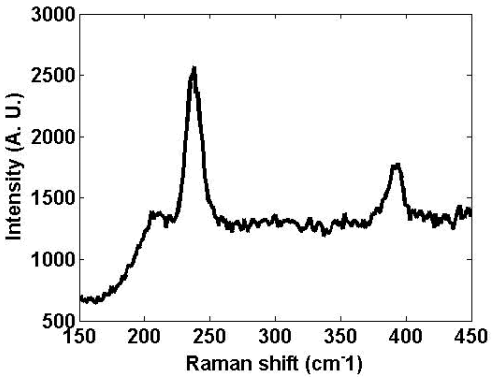

FIG. 4: Raman spectrum of the CdSe quantum dots on indium tin oxide coated glass substrate at room temperature excited with a 325-nm laser. LO peaks are at 237.5 cm^{-1} and 390 cm^{-1}. The SO mode is at 204 cm^{-1}.

cm^{-1}.

A theoretical investigation of the phonon modes in CdS and CdSe quantum dots is performed following Klein's analysis [17] of the LO and SO vibrational eigenmodes in a semiconductor sphere. The interaction of electrons with optical phonon modes in a polar semiconductor material is termed as Fröhlich interaction. The lattice vibrations produce an electric polarization $\mathbf{P}$ in the medium. This polarization is related to the electric potential$\phi$by the following equation [18, 19]:

$$\nabla^2\phi(r) = 4\pi\nabla\cdot\mathbf{P} \tag{1}$$

The LO and the SO modes are calculated with the help of the dielectric continuum model.

Following Mori and Ando [20] or Licari and Evrard [21], we start with the following equations:

$$\mathbf{D} = \varepsilon\mathbf{E} = \mathbf{E} + 4\pi\mathbf{P} \tag{2}$$

$$\mathbf{E} = -\nabla\phi \tag{3}$$

$$\nabla\cdot\mathbf{D} = 0, \tag{4}$$

where $\mathbf{D}$ is the electric displacement, $\mathbf{E}$ is the electric field, is dielectric constant, $\mathbf{P}$ is the polarization density andϕ is the electric potential. It follows directly from equations (2) and (4)

$$\varepsilon\Delta\phi = 0 \tag{5}$$

There are two possible ways to solve this equation. For one solution, $\varepsilon = 0$, which corresponds to the confined modes. The other way to solve this equation is by taking

$$\Delta\phi = 0, \tag{6}$$

which will provide the surface modes.

Case I: Confined phonon modes

$\varepsilon = 0$ corresponds to the LO modes of eigen-frequencies $\omega_{LO.}$˜The eigen-functions may be written in the spherical polar coordinates as

$$B_k j_l(kr) Y_l^m(\theta, \varphi) \tag{7}$$

$$\phi(r) = \sum_{l,m} \sum_k B_k j_l(kr) Y_l^m(\theta, \varphi), \tag{8}$$

where Y_l^m˜are spherical harmonics and $j_l(kr)$ are spherical Bessel functions of order l. The boundary condition matching requires the continuity of ϕ at the interface and also the continuity of the normal component of D at the interface. ϕ vanishes outside the quantum dot and at its surface. Then we have the condition

$$j_l(kR) = 0, \tag{9}$$

where $k = \frac{\alpha_{n,l}}{R}$ and is the nth zero of the spherical Bessel function of order l. Thus, the confined modes have discrete values. For l= 0, using the properties of spherical Bessel functions [22, 23], we get the following relation:

$$\tan\alpha_n = \alpha_n, \text{ for n = 1, 2, 3...} \tag{10}$$

$$\omega_n^2 = \omega_L^2 - \beta_L^2 \left(\frac{\alpha_n}{R}\right)^2, \tag{11}$$

where is a parameter describing the dispersion of the LO phonon in the bulk material, is LO phonon frequency in the bulk and is confined LO phonon frequency in the quantum dot. The confined LO mode energies are plotted in Fig. 5 and Fig. 6 for different radii of CdS and CdSe quantum dots, respectively. The parameters used for the calculation are listed in Table I.

From Fig. 5, the red shift of the LO peak is ∼3 cm^{-1} for CdS quantum dots of size 3 nm, which agrees well with the experimental value of the red shift. From Fig. 6, the shift is 0.2 cm^{-1} for CdSe quantum dots of size 7 nm.

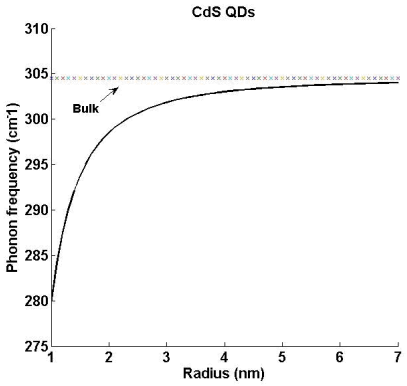

FIG. 5: LO phonon frequencies for different radii of CdS quantum dots (dark line). The bulk LO frequency is at 304.5 cm^{-1} (crossed line).

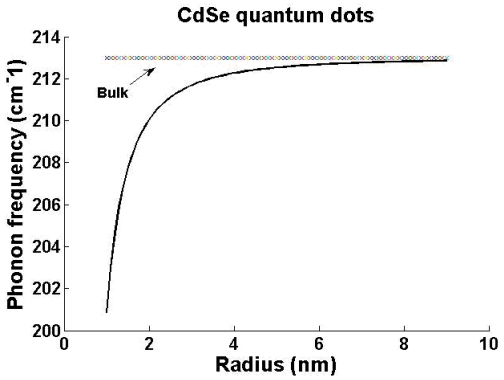

FIG. 6: LO phonon frequencies for different radii of CdSe quantum dots (dark line). The bulk LO frequency is at 213 cm^{-1} (crossed line).

Case II: Surface modes

For surface modes

$$\Delta\phi = 0 \tag{12}$$

The eigenfunctions that satisfy this condition are given as

$$\phi(r) = A_{l,m} r^l Y_l^m(\theta,\varphi) \qquad \text{for r} < \text{R} \tag{13}$$

$$\phi(r) = B_{l,m} r^{-l-1} Y_l^m(\theta,\varphi) \qquad \text{for r} > \text{R} \tag{14}$$

By matching the boundary conditions, we get

$$\frac{\varepsilon_1(\omega_l)}{\varepsilon_2(\omega_l)} = -1 - \frac{1}{l} \tag{15}$$

where l= 1, 2, 3... and and are the dielectric constants in the quantum dot and the matrix surrounding it, respectively. The dielectric constants can be written as

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\left(\omega^2 - \omega_{LO}^2\right)}{\left(\omega^2 - \omega_{TO}^2\right)}, \tag{16}$$

where ε_∞ is the high-frequency dielectric constant. When the matrix surrounding the quantum dots is non polar, there is only one SO mode for a given (l, m). Using eq. (16), the surface phonon energies of different quantum dots in different matrix materials can be calculated for different quantum numbers. For CdSe and CdS quantum dots the values of the parameters used to calculate the SO mode energies are listed in Table I. In CdS quantum dots the SO modes were not observed experimentally. In CdSe dots the SO1 mode is observed at 204 cm^{-1}. There is a close agreement between the calculated value of the SO1 frequency of 204.8 cm^{-1}(Table I) for CdSe quantum dots and the experimental

value (Fig. 4) of 204 cm^{-1}. Also from Fig. 5, the calculated red shift of the confined LO peak is 3 cm^{-1} for CdS quantum dots, which agrees with the experimental value of the red shift of 3 cm^{-1} of the confined LO frequency from the bulk value shown in Fig. 2.

TABLE I: Parameters of CdS and CdSe quantum dots used for the calculations of the confined LO mode and the SO mode frequencies.

	CdS	CdSe
ε_∞	5.3	6.1
ε_d	1	1
$\beta_L(ms^{-1})$	5.04×10^{3} [a]	2.969×10^{3} [b]
$\hbar\omega_{LO}$(meV)	37.75 (304.5cm^{-1}) [c]	26.54 (213 cm^{-1}) [d]
$\hbar\omega_{TO}$(meV)	29.38 (237 cm^{-1}) [c]	21.49 (173.3 cm^{-1}) [e]
$\hbar\omega_{SO1}$, l = 1 (meV)	35.66 (287.6 cm^{-1})	25.388 (204.8 cm^{-1})
$\hbar\omega_{SO1,}$l = 2 (meV)	36.07 (290.9 cm^{-1})	25.623 (206.7 cm^{-1})
$\hbar\omega_{SO1,}$l = 3 (meV)	36.23 (292.2 cm^{-1})	25.889(208.8 cm^{-1})

[a] Reference [23]
[b] Reference [24]
[c] Reference [25]
[d] Reference [24]
[e] Reference [26]

IV. CONCLUSIONS

Confined LO phonon modes are studied in CdS and CdSe quantum dots using Raman scattering measurements. In CdS dots, the measured LO frequency is less compared to that in the bulk because of the phonon confinement effect. In CdSe dots, LO modes are measured at frequencies higher than the bulk LO mode. The possible origin of these high-frequency LO modes is the manifestation of the surface states in the phonon density of states in these dots. The surface reconstruction gives rise to modified surface states. A dielectric continuum model is used to calculate the confined LO and SO modes in the two kinds of quantum dots. The red shift in the LO phonon frequency in CdS quantum dots due to phonon confinement agree with the calculated value.

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