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Pressure Raman scattering of CdTe quantum dots

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A series of zinc-blende CdTe quantum dots in glass was investigated using Raman scattering and luminescence. The dot size was controlled by varying the annealing conditions. Luminescence was employed as a probe for quality of the sample and its adequacy for resonance. Resonant Raman spectra at the lowest confined energy levels of the quantum dots were obtained in function of the pressure in the range 1 bar to 4.6 GPa. The upper limit was established by a phase transition probably to NaCl structure, simultaneous with disappearance of Raman signal. In the latter phase, first-order Raman scattering is forbidden. The Grüneisen parameter for the LO phonon of CdTe quantum dots is given. [S0163-1829(97)04712-7]

I. INTRODUCTION

It was established a number of years ago that finite-size effects can have a strong influence on the electronic properties of crystals.[1,2] The confinement energies are increased with respect to bulk values and a series of discrete states are available in the conduction and valence bands, allowing for electron-hole transitions to occur. Because of the distribution of quantum dot sizes the absorption spectrum occurs as broadbands, rather than discrete lines, as a consequence of the superposition of the contribution from each individual dot. The absorption bands shift toward the blue end of the spectrum with decreasing size. This fact offers the attractive possibility of tuning resonant conditions by just a choice of synthesis parameters.

The task is particularly easy for CdTe nanocrystals embedded in glass matrices, for which the size depends only on heat treatments. A recent work reports on the fabrication of CdTe quantum dot in glass of varying size, with an average diameter ranging between 2.4 and 12.5 nm, whereas the corresponding lowest absorption peak energy fall in the range 2.93–1.60 eV.[3] The corresponding transition energies can be calculated by using a multiband envelope-function model.[4,5] This formalism proved effective in determining quantum confined levels of CdTe quantum dots.[6]

While confinement effects on electronic properties are well understood in CdTe, there is a lack of information regarding the vibrational properties. The phonon confinement should affect the phonon energy in addition to size-dependent strain.[7] In order to describe the phonon localization properly, the effect of strain should be taken into account. The hydrostatic component of the strain is given by the Grüneisen parameter γ, whose value is available for a number of semiconductors.[8] However, to the best of our knowledge, no such value has been reported to date for CdTe. A possible cause of this is that weak Raman lines of bulk CdTe may merge into strong background from reflections on the pressure cell windows. To overcome this difficulty, resonant Raman scattering should be tried.

In this work we studied a series of CdTe quantum dots imbedded in borosilicate glass, with varying dot sizes. Luminescence, which is highly sensitive to dot sizes, was used as a tool to choose the appropriate sample for resonant Raman measurements. The choice fell in the sample with the lowest absorption peak position as close as possible to the energy of the exciting radiation. The overlap of closed spaced electronic transition energies, and the nonuniformity of size, ensures resonance over a broad region.

II. EXPERIMENT

The measurements were performed in CdTe nanocrystals imbedded in borosilicate glass. The semiconductor constituents, during the process of preparation of the glass, do not form crystallites. Quantum dots are produced by a subsequent heat treatment. The average size of the dots is time and temperature dependent. The glass was prepared by melting a mixture of SiO_2, B_2O_3, Na_2CO_3, and ZnO as described in Ref. 9. CdO and Te were added in a volume fraction of 1% in the mixture. A series of five samples was obtained by annealing at 580 °C for a period of time varying between 10 and 60 min. Also, a special sample was prepared at a lower annealing temperature, 560 °C for 22 min, to be of use in the pressure runs. Photoluminescence spectra were obtained by using a 488.0-nm line of an Ar-ion laser as excitation. Detection was achieved with a C31034A photomultiplier. A backscattering geometry was used in the Raman measurements. The scattering was excited with the 514.5-nm line of an Ar-ion laser at low power to avoid darkening of the dots. A bulk CdTe sample oriented along the [001] crystalline direction was used for comparison purposes. A Jobin-Yvon T64000 Raman system equipped with N_2 cooled charge-coupled device (CCD) was employed for detection. The pressure was applied with a diamond-anvil cell loaded with a 4:1 mixture of methanol:ethanol as transmitting fluid. The pressure calibration was obtained with the ruby fluorescence

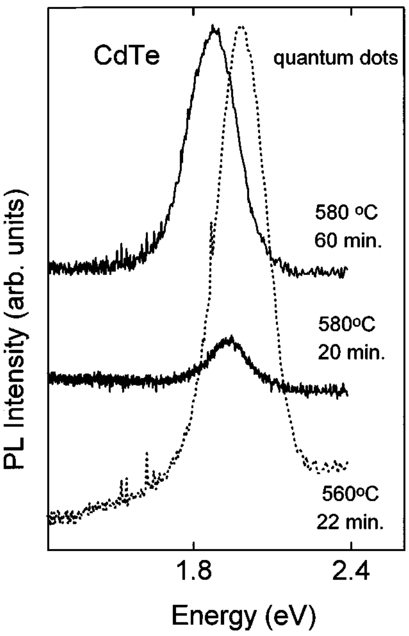

FIG. 1. Luminescence spectra of CdTe quantum dots for different annealing conditions.

method.[10] All the measurements were performed at room temperature. The Raman shifts were calibrated with the line $\lambda = 533.1$ nm of a Ne lamp.

III. RESULTS AND DISCUSSION

Luminescence spectra for samples treated at a fixed temperature, $T = 580$ °C, and several annealing times were obtained. The spectra of representative samples are given in Fig. 1. Corresponding annealing conditions are marked in the right side of the spectra. The photoluminescence intensity and peak position are dependent on the annealing time. The peak displaces toward lower energies and the intensity increases with time of heat treatment. The redshift of the luminescence is related to the increase of the average size of the nanocrystals.[11] Figure 1 also illustrates the enhancement of luminescence with increased density of dots. The interest here is to produce maxima density of quantum dots with smallest possible sizes. For annealing times shorter than 20 min, we observed a band-to-band emission as a very weak line and the emission from traps as the major feature in the spectrum (not shown here). A good compromise was obtained with annealing at 560 °C for 22 min, as illustrated by the dotted curve of Fig. 1. Therefore, the sample selected for the Raman measurements was the one treated at 560 °C for 22 min, which will be referred to as CdTe quantum dots hereafter.

The Raman spectrum of CdTe quantum dots is shown in Fig. 2, lowest curve. Also included is the spectrum of CdTe bulk for comparison purposes. Three peaks are seen in this spectrum at 120.6, 139.7, and 164.3 cm^{-1}. The highest-frequency peak corresponds to the LO mode of the CdTe bulk, the only allowed mode in the geometry employed. The two lowest frequency peaks correspond to the modes A_1 and E of Te, respectively. They were present even after the sample was subjected to an special chemomechanical polish to remove Te from the surface.[12] This fact shows the presence of Te precipitates in the CdTe bulk sample. The spectrum of CdTe quantum dots consists of a single line at 161.7 cm^{-1}. This peak corresponds to the LO mode. The observed redshift of this peak will be discussed in detail in a forthcoming publication.

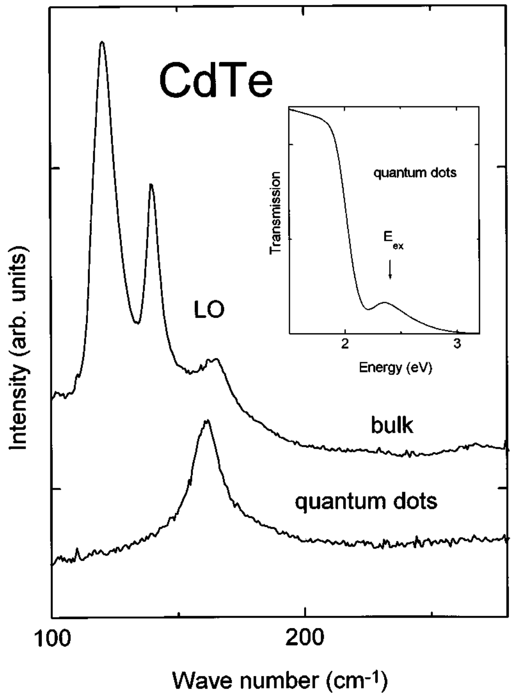

FIG. 2. Raman spectra of CdTe bulk and quantum dots. The inset gives the transmission for the sample annealed at 560 °C for 22 min. E_{ex} indicates the excitation energy.

The spectrum is puzzling at a first glance, because of the absence of a peak at the TO frequency value. A previously published work on microcrystalline CdTe reported on the observation of both LO and TO phonons.[13] The puzzle is solved on reasoning on the basis of resonance. The LO mode is more strongly resonant than the TO, since it may contain, in addition to the dipole moment effects, contributions attributed to the electron-phonon Fröhlich interaction. Recent observations show strongly enhanced LO intensities against practically unchanged TO magnitudes in the CdTe bulk on resonance at $E_0 + \Delta_0$.[14]

A similar effect may be assumed as the responsible for the exclusive LO scattering of our quantum dots. The lowest confinement energies for these quantum dots are grouped around 2.34 eV, as indicates the peak position in transmission (see the inset of Fig. 2). According to a simple effective-mass model, this energy value corresponds to the heavy-hole–electron transition.[1] This oversimplified picture hinders a description of the several quantum states in both valence and conduction bands. A more elaborated formalism based on the multiband envelop theory propose a more realistic model for quantum dot systems.[4,5] The treatment imposes band-coupling effects at the highest valance subbands leading to a mixed heavy-hole–light-hole character. The energies of those bands are close together for the dot sizes of our samples. Also, considering that the dot radii have a distribution of about 6–10 %, there is a spread of energies into a

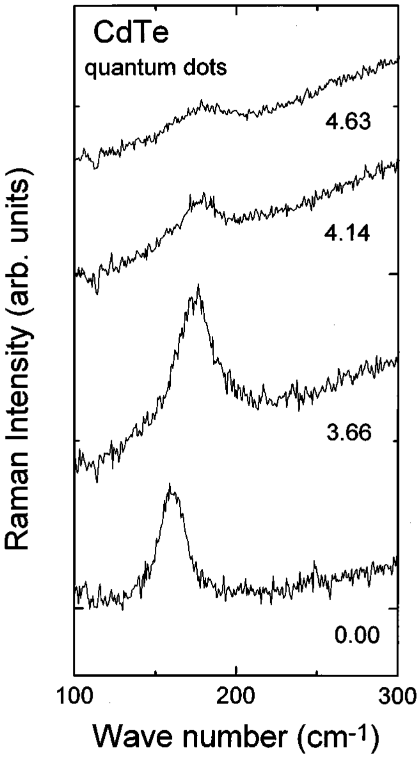

FIG. 3. Raman spectra of CdTe quantum dots for four pressure values. The numbers at the right side of the spectra are pressure values in units of GPa.

broad region. Those are the reasons why a wide range of energies centered at the value of the lowest transmission peak is available to produce resonance. The incident radiation utilized here ($E_{\mathrm{ex}}=2.41$ eV) fulfills the described resonance condition (see Fig. 2).

Resonant Raman spectra taken at four different pressures are shown in Fig. 3. The numbers labeling the spectra in this figure are pressure values in units of GPa. It is possible to observe in this figure that at any pressure value the spectrum consists of a single peak corresponding to the LO mode. The LO frequency shifts upward with increasing pressure, at a rate given further on. We will first discuss the behavior of the intensities. The integrated intensities remain practically constant in the range comprised between atmospheric pressure and 3.66 GPa. Comparison of the lowest curve of Fig. 3 and that of $P=3.66$ GPa illustrates those observations. On increasing the pressure beyond 4 GPa the intensity diminishes drastically up to a near disappearance for $P\sim4.6$ GPa. The upper curves of Fig. 3 show the decreasing intensity for two close spaced pressure values. In order to interpret this near–disappearance of the Raman line we compare our results with those found for bulk CdTe.

In bulk CdTe a structural phase transition occurs at 3.9 GPa as indicate the results from several optical[15,16] and x-ray diffraction studies.[17] The change is from zinc-blende to rocksalt structure, and occurs simultaneously with a drastic decrease in volume. This structural phase transition in bulk CdTe quenches the luminescence beyond 3.9 GPa as a consequence of a large number of defects produced by the discontinuous change in volume.[15,16] In the NaCl phase, first-order Raman scattering is forbidden by symmetry. For this reason a disappearance of the Raman peak is expected upon crossing from zinc-blende to NaCl structure. Another phase, reported as a cinnabar structure,[17] was found between 3.6 and 2.7 GPa (as a single phase on pressure decrease). The details on this latter transformation are omitted because they were found to be of no consequence to the present work. Considering those facts, we believe that the near disappearance of the Raman line of the quantum dots at $P\sim4.6$ GPa is related to the zinc-blende–NaCl phase transition.

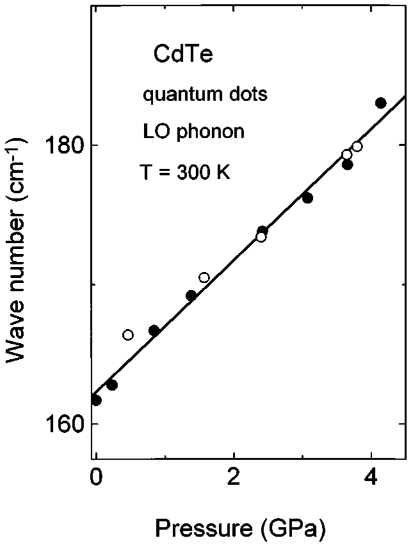

FIG. 4. Pressure dependence of the LO-phonon energy for CdTe quantum dots. The closed (open) symbols are for increasing (decreasing) pressure runs.

It is worth mentioning, at this point, that the Raman intensity of the quantum dots was observed to recover upon reducing the pressure below 4.0 GPa. These behavior is presented in Fig. 4, where we plot the frequency of the LO phonon of CdTe quantum dots versus pressure both on increasing and decreasing pressure runs. The closed symbols are for data taken rising the pressure and the open symbols are representative of data taken on releasing the pressure. For clarity's sake, not all the experimental points were included. The frequency is observed to increase linearly with pressure. The solid line is a least-square fitting of the data to the equation

$$\omega=\omega_0+\alpha P. \tag{1}$$

This fitting gives $\omega_0=162.8$ cm^{-1} and $\alpha=4.78$ cm^{-1}/GPa. The decreasing pressure runs give frequencies which fit the same frequency versus pressure plot as that of increasing pressure runs. Our result for the pressure coefficient together with the bulk modulus reported elsewhere for the zinc-blende CdTe, $B_0=43.7$ GPa,[17] allowed for the calculation of the Grüneisen parameter for the CdTe LO phonon as $\gamma=1.28$. We believe that this value does not differ appreciably from the bulk, thus providing valuable information for size depend lattice strains in low-dimensional CdTe-based systems.

IV. CONCLUSIONS

In conclusion, we measured photoluminescence of a series of CdTe nanocrystals embedded in borosilicate glass, with varying dot sizes. From the analyses of photoluminescence a sample was chosen to perform resonant Raman scattering. The dependence of the Raman bands on hydrostatic pressure allowed us to determine the Grüneisen parameter. This value is helpful in distinguishing between quantum-size effects and strain-induced shifts in the phonon energy of low-dimensional systems. The CdTe LO-phonon pressure coefficients were not available to date, either for bulk or any low-dimensional system, to our knowledge.

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