Vol 13 No 10, October 2004
1009-1963/2004/13(10)/1753-05

Chinese Physics

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and IOP Publishing Ltd

Raman spectra of ZnSe nanoparticles synthesized by thermal evaporation method

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(Received 13 February 2004; revised manuscript received 29 March 2004)

ZnSe nanoparticles were synthesized by using a thermal evaporation method for a vapour phase reaction of zinc and selenium sources. The sample was characterized by XRD, TEM, HRTEM and Raman spectroscopy. Raman spectra of longitudinal-optical (LO) like mode was analysed by a macroscopic continuum dielectric model. Large broadening of LO-mode is homogeneous and comes from the relaxation of the phonons at the interface and contribution of defects. Surface modes give the main contribution to the asymmetry of the lineshape.

Keywords: ZnSe nanoparticles, Raman spectra, macroscopic continuum dielectric model(MCDM), surface modes

PACC: 6322, 7830L, 6830

1. Introduction

Nanomaterials of different II–VI semiconductors have elicited renewed interest of the great potential for optical device applications due to their nonlinear optical properties.[1–4] The quantum confinement effects are the subjects of much current research. Raman spectroscopy, which has been recognized as an important structural probe, provides a fast convenient method for the study of vibrational and structural properties of low-dimension materials.[5,6]

Many researches have been done on the phonon properties of other II–VI nanomaterials such as CdS,[7,8] CdSe[9] and CdTe.[10] But the size-effects on their phonon modes and on the electron–phonon interactions are still somewhat controversial. de Paula *et al*[10] observed no shift of the LO-phonon frequency with the experimental resolution of 1cm^{-1} when studying CdTe quantum dots with mean-radius of 3.6nm. Sarigiannis *et al*[1] also observed no shift of the phonon frequency when discussing the LO mode of vapour-phase-grown ZnSe nanoparticles with diameters of about 4nm. But a microcrystal model (MCM)[11] was used in their discussion to analyse the LO mode which gave an expected redshift of about 10cm^{-1} and the asymmetric broadening was explained to be due to the relaxation in the q-vector selection rule. No shift of LO mode was explained to be due to the existence of particles with a distribution of various sizes. However, the lineshapes of LO mode are well described as Lorentzian by Hwang and Park[12] when studying CdSe quantum dots with a diameter of 2.6nm, and the Lorentzian surface modes have contribution to the asymmetry of LO mode.

To describe the scattering by the confined phonon mode of Raman spectra, a macroscopic continuum dielectric model (MCDM) was proposed to study the polar optical vibrations in nanostructures.[13] It uses eigenstate modes of phonons confined in a sphere instead of superposition of all phonons near k=0 to describe the contribution of relaxation of phonon momentum conservation on the Raman spectra. This model was successfully used by Vasilevskiy *et al*[7,8] to analyse the correlation between the lineshape of the Raman spectra and the crystalline quality of the semiconductor quantum dots and gave satisfactory results.

In the present work, we study the reduced space dimension effects of ZnSe nanocrystals on the Raman lineshape. To describe the experimental Raman lineshape, we use MCDM discussed above to analyse LO mode. Our discussion shows that the relaxation of phonon momentum conservation has little contribution to the asymmetry of lineshape because of the

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small dispersion of phonons with wave vector q between 0 and π/R_0. Large homogeneous broadening originates from phonon relaxation at the interface. Surface modes are also considered to explain the asymmetry of the lower frequency region.

2. Experiment

The ZnSe nanoparticles were grown by a vapour deposition method. Two quartz boats filled with pure zinc and selenium powders were located at different temperature zones in a tube furnace with the zinc and selenium source near a water-cooled copper collector at one end and the gas input on the other end. The tube was evacuated to and maintained at about 20KPa during the whole growth process. The system was raised to 700°C and maintained for 60min and a continuous Ar flow of 50 sccm was input into the system during the growth. After the furnace cooled down to room temperature, a yellowish layer covered the copper collector, which was collected for further analysis. The phase of the as-grown sample was studied by x-ray diffraction. The morphology of the sample was analysed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The energy dispersive spectroscopy technique was used to assess the chemical composition of the nanoparticles.

Micro-Raman spectra were measured in a back-scattering geometry at 273K under the excitation of a solid-state laser with a 532nm wavelength. The scattered light was dispersed through a Jobin Yvon HRD1 monochromator and a TE-cooled charge-coupled-device (CCD) was used as detector. No polarization was considered. The monochromator was calibrated by using the strong plasma lines of the He–Ne laser. The low excitation power for the laser was used to avoid local heating of the sample. The slit width of the monochromator was set to 100μm. The spectral resolution at this slit is about 2cm^{-1}.

3. Results and discussion

The x-ray diffraction (XRD) pattern of the sample is shown in Fig.1, which demonstrates that the sample has a zinc-blende crystal structure. A TEM image (Fig.2) provides the general morphology of the as-grown aggregates. The aggregates consist of polycrystalline ZnSe nanoparticles with diameters of about 80nm. Many HRTEM micrographs (not shown) indicate that the polycrystalline nanoparticles were formed from coagulation of smaller nanocrystal grains with a characteristic size about 4nm.

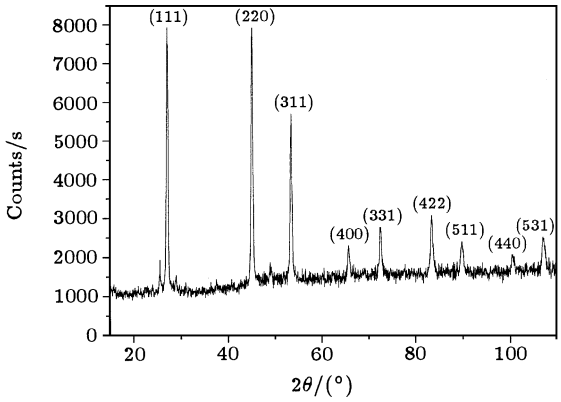


Fig.1. X-ray diffraction pattern of the as-synthesized samples. Indices of the peaks are specified above the peaks.

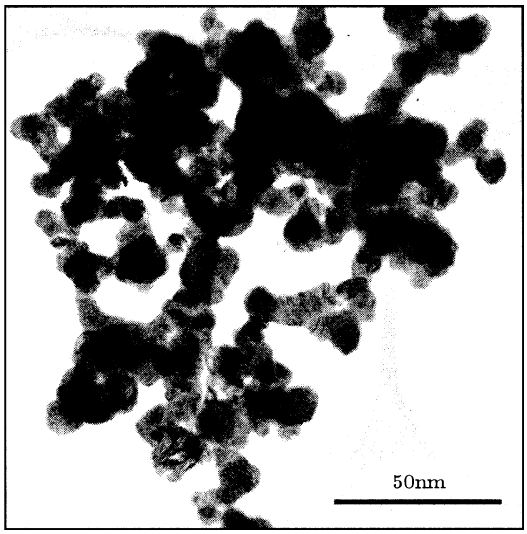


Fig.2. Typical TEM images of the nanoparticles synthesized at 700°C.

Figure 3(a) shows experimental and calculated Raman spectra of the ZnSe nanoparticles. Raman spectrum of the bulk crystal was also obtained for comparison. In the experimental spectra, a frequency-dependent background of the form $C + D\omega$ owing to fluorescence was subtracted. The parameters C and D were obtained by fitting the data away from the peaks.[14]

In Fig.3(a), we provide the Raman spectra of as-grown ZnSe nanoparticles and the bulk crystal. Spectral intensity is normalized by the LO phonon peak intensity for comparison. No obvious peak shift of nanoparticles from that of bulk material is observed for both TO and LO phonon modes. Large homogeneous spectral broadenings are obvious.

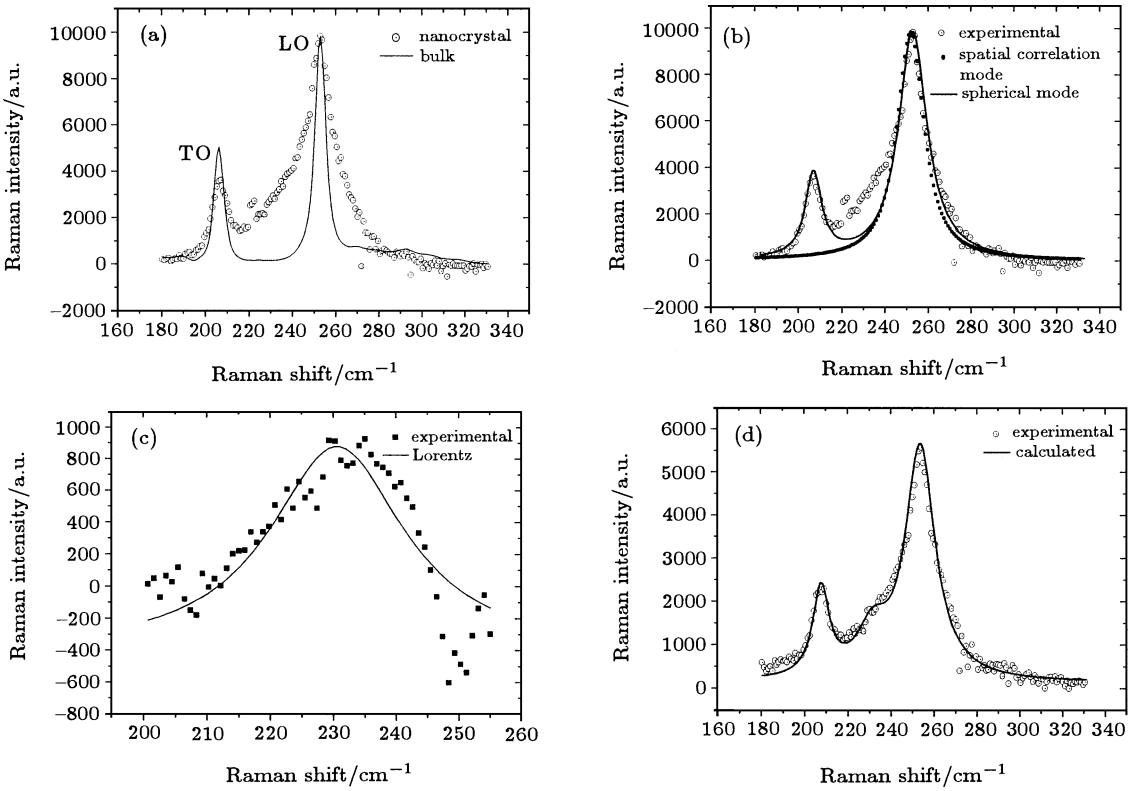


Fig.3. (a) Raman spectra of the as-grown ZnSe nanocrystal (circles) and bulk material (solid line); (b) Raman spectra of the as-grown ZnSe sample (circle) and theoretical results of LO mode; (c) Raman lineshapes for surface modes (dark dots) and Lorentz fitting (solid line); (d) Experimental (circles) and theoretical (solid line) Raman spectra of the as-grown ZnSe nanocrystals.

From the XRD analysis, as-grown nanoparticles have almost the same lattice constant as that of bulk materials. So here we do not consider the effect of the lattice contraction.

For the bulk material, the phonon eigenstates are plane waves, therefore the usual q=0 momentum selection rule of the first-order Raman spectrum can be satisfied.[15] However, when the size of the material decreases to the nanoscale, momentum conversation rules will be relaxed and the phonons at $q \neq 0$ may have contribution to the Raman spectra. According to the uncertainty principle of phonon wave vector,[16] the phonon within the wave vector near π/R_0 will have influence on the lineshape of the Raman spectra. Here we analyse our experimental data in terms of the macroscopic continuum dielectric model [13] on the basis of a continuum equation of motion for the relative displacement of two sublattices of a zinc-blende structure semiconductor. For nanocrystals with diameter of about 4nm, the optical vibrations are considered to be confined to the nanocrystals with a spherical shape and are assigned an equivalent wave vector[13,17]

$$q_n = \frac{\mu_n}{R_0}, \qquad (1)$$

where μ_n is the nth node of the spherical Bessel function j_1, and R_0 is the particle radius.

The dispersion relation of optical phonon for bulk material we used in our discussion is as follows:[18]

$$\omega^2(q) = A + [A^2 - B(1 - \cos(aq))]^{1/2}, \qquad (2)$$

where A=3.2×10^{4}cm^{-2} and B=4.5×10^{8}cm^{-4}, a is the lattice constant of Zinc-blende structure of ZnSe bulk crystal. Expanding expression (2) in a Taylor series, we obtain the quadratic negative bulk dispersion:

$$\omega^2(q) = \omega_{\rm LO}^2 - \beta_{\rm LO}^2 q^2, \qquad (3)$$

where $\omega_{\rm LO}$ and $\beta_{\rm LO}$ are the bulk LO phonon frequency and LO phonon dispersion curve bending parameter estimated from the phonon dispersion relation (2) of the corresponding bulk material, respectively; the corresponding values are 253cm^{-1}and 33.6cm^{-1}·nm, respectively. From Eqs.(1) and (3), we have the frequencies 251 and 246cm^{-1}, for n=1,2 mode, respectively.

The Raman cross-section can be written in the

following form:[7]

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}\omega_\mathrm{s}} = \frac{\omega_\mathrm{i}\omega_\mathrm{s}^3 v^2}{\pi c^4}[n(\omega)+1] \times \left\{ -\mathrm{Im}\sum_v \frac{|\Theta_v|^2}{\omega-\omega_v+\mathrm{i}\Gamma_\mathrm{LO}/2} \right\}, \quad (4)$$

where v is the unit cell volume, i and s correspond to the incident and scattered light, respectively, $n(\omega)$ is the Bose factor, $\omega=\omega_\mathrm{i}-\omega_\mathrm{s}$, Γ_LO is the damping parameter, n enumerates phonon eigenstates and Θ_ν is a scattering matrix element.

The scattering matrix Θ_n describes the non-polar (via the deformation potential) and polar (via the Fröhlich electric field) scatterings. In our experiments, the excitation energy (2.33eV) is below the absorption edge of nano ZnSe; details of the scattering matrix Θ_n calculations can be seen elsewhere.[7,8] For ZnSe nanocrystals, calculations show that the n=1 mode has the strongest cross section. The intensity of the n=2 mode is only 3.5% of the n=1 mode, and the higher n modes are even much weaker because of the scattering amplitude cancellations.

So here we just used n=1,2 mode and damping parameter Γ_LO=16cm^{-1}, to fit the LO mode of experimental data. In Fig.3(b) the theoretical line obtained is shown as the solid line. The peak position of the theoretical result (251cm^{-1}) has a little discrepancy with the experimental data (253cm^{-1}), which is almost the same as the peak of the bulk material. The discrepancy may come from existence of grains with diameters larger than 4nm, which can be demonstrated by our HRTEM result. In order to compare the lineshape with the experimental result, we shift the theoretical spectra such that the theoretical peak coincides with the experimental one. There is good agreement in spectral features between experimental and theoretical lineshapes of the LO mode.

The results demonstrated that the theoretical lineshapes are almost Lorentzian and the broadening is homogeneous. In order to compare our discussion with others about nanocrystal of II–VI compounds, we also analyse our Raman spectra with another phenomenological model, which is proposed by Richter *et al*[11] and has been used by most experimentalists. A Gaussian spatial correlation function $\exp(-2r^2/R_0^2)$ has been used to account for q-vector relaxation related to the size effect. Then the Raman intensity $I(\omega)$ can be written as[11]

$$I(\omega) \propto \int \frac{\exp(-q^2R_0^2/4)}{[\omega-\omega(q)]^2+(\Gamma/2)^2}\mathrm{d}^3q, \quad (5)$$

where $\omega(q)$ is the phonon dispersion curve described by Eq.(2), Γ is the homogeneous broadening of nanoparticles here used in our calculation and its value is 14cm^{-1} instead of the natural width (6cm^{-1}) of bulk material used by others.[1,18]. In Fig.3(b), the theoretical result is shown as the dashed line.

The theoretical spectra calculated by the two modes almost coincide and both give good reproduction of lineshape of LO phonon mode. From Eqs.(2) and (3), we can learn that the bulk LO phonon dispersion curve of ZnSe is relatively flat near k=0 (β_LO is rather small). Although the relaxation of the q=0 selection rule has contribution to the lineshape, it does not play the main role in the large homogeneous broadening and asymmetry of Raman spectra. That is why we use 14cm^{-1} instead of 6cm^{-1} as the value of Γ when we calculated the lineshape of Raman spectra. Large homogeneous broadening of Raman spectra seems to be a common characteristic for quantum dots of nanomaterials with small diameters in the II–VI group.[7,12,17] The reduced dimensions of nanocrystals decrease the mean free path of phonons and the phonons confined in the nanocrystals frequently collide and relax at the interface. Lattice distortion and structure defects are the common features of most nanostructured materials which also result in shortening of the lifetime of phonons and contribute to the large homogeneous broadening.[12] So some authors just analysed LO modes of quantum dots with a mean diameter of 2.6nm by a Lorentz function and gave good reproduction of their experimental spectra.[12,19]

For the TO mode, the discussion is similar to that of the LO mode, so here we just use a Lorentz function with the peak at 207cm^{-1} and width of 9cm^{-1} to fit the TO mode. But when we investigate the region with a frequency about 230cm^{-1}, a large discrepancy still exists. Figure 3(c) shows the difference between the experimental spectrum and the overall TO and LO theoretical lineshape. Here we designate it as surface modes.

From the theoretical point of view, some surface modes should be Raman active. In order to give a qualitative analysis, here we consider a sphere of radius R_0. If the number of surface modes is proportional to $\frac{4}{\pi}R_0^2$, the number of LO modes will be proportional to $\frac{4R_0^3}{3\pi}$. The ratio is $3/R_0$. So for bulk material the surface modes are very few compared with bulk modes, and they could not be observed. But for

small nanocrystals, especially when ionic microcrystal size is smaller than the wavelength of the incident light in the crystal, surface modes can be observed.[20]

For bulk materials the frequencies of surface modes are given by[13]

$$\omega^2 = \omega_{\rm TO}^2 \frac{\varepsilon_0 l + (l+1)\varepsilon_\infty}{(2l+1)\varepsilon_\infty}, \quad (l = 1, 2, 3, \cdots), \qquad (6)$$

where ε_0 and ε_∞ are the semiconductor static and high-frequency dielectric constants, l is the order of the spherical harmonics. For l=1 the so-called Fröhlich frequency $\omega_{\rm F}^2 = \dfrac{\omega_{\rm LO}^2 + 2\omega_{\rm TO}^2}{3}$ is derived. Using the ZnSe parameters,[21] we obtain for the lowest (l=1) and highest ($l \to \infty$) modes $\omega_{\rm F}$=223cm^{-1} and $\omega_{\rm SM_\infty}$=231cm^{-1}. As the size of the material decreases, the surface phonon frequency will be blue shift and broadening,[12] so the Fröhlich frequency for a finite R_0 lies above $\omega_{\rm F}$ and below $\omega_{\rm LO}$.[8] The shoulder between the TO and LO peak are due to scattering from Fröhlich mode and all the other surface modes.[10] Because of the weaker intensity here we just use one Lorentz function to describe the effect of surface modes in Fig.3(c) and the spectrum shown by dark dots is the difference between the experimental spectrum and fitting result by MCDM. Figure 3(d) gives the result when we consider all factors discussed above. Its theoretical fit (solid line) is a sum of the contributions of the confined LO modes and surface modes, which shows that our model gives a good reproduction of the Raman spectra of ZnSe nanoparticles.

4. Conclusion

In summary, because of the small dispersion of optical phonons near q=0, asymmetric broadening of the longitudinal mode caused by relaxation of the q=0 selection rule is rather small. The observed lineshape of LO mode is indicative of homogeneous broadening. The broadening originates from the boundary relaxation of phonons at the interface between different quantum dots. For small nanocrystals surface modes with lower frequency than the LO mode can be observed, and they give the main contribution to the asymmetry broadening of Raman spectra.

Acknowledgements

Huizhi An is grateful to Professor Shang-Fen Ren and Professor Wei Cheng for careful reading of the transcript and helpful comments.

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