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Citation: Applied Physics Letters 91, 181913 (2007); doi: 10.1063/1.2805192
View online: http://dx.doi.org/10.1063/1.2805192
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Reducing exciton-longitudinal-optical phonon interaction with shrinking ZnO quantum dots

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(Received 11 September 2007; accepted 12 October 2007; published online 1 November 2007)

The exciton-longitudinal-optical-phonon (LO-phonon) interaction was observed to decrease with reducing ZnO particle size to its exciton Bohr radius ($a_B$). The unapparent LO-phonon replicas of free exciton (FX) emission and the smaller FX energy difference between 13 and 300 K reveal decreasing weighting of exciton-LO phonon coupling strength. The diminished Fröhlich interaction mainly results from the reducing $a_B$ with size due to the quantum confinement effect that makes the exciton less polar. © 2007 American Institute of Physics. [DOI: 10.1063/1.2805192]

During the last decade, zinc oxide (ZnO) has received much attention because of its wide band gap and large binding energy ($E_b \approx 60$ meV). Optical and physical properties of semiconductor quantum dots (QDs) have also devoted considerable efforts to study due to their potential applications to light-emitting diodes, optically pumped lasers, and other electronic devices. Although a large number of researches on II-VI QDs and III-V QDs have been published, the properties of ZnO QDs have not been studied as completely as other materials.

The interaction between exciton and longitudinal-optical (LO) phonon has a great influence on the optical properties of polar semiconductors. Ramvall et al. reported a diminishing temperature-dependent shift of the photoluminescence (PL) energy with decreasing GaN QD size caused by a reduction of the LO-phonon coupling. In our previous work, the resonant Raman scattering (RRS) of various ZnO QD sizes reveals that decrease of $E_{2LO}/E_{1LO}$ with decreasing particle sizes gives an evidence for the reduction of exciton-LO phonon interaction with decreasing QD size. Chang and Lin theoretically reported that the exciton LO-phonon interaction energy $|E_{\text{ex-phon}}|$ is evaluated as functions of electric field strength and the size of the quantum dots. The field enhanced by reducing the separation between electron and hole would increase $|E_{\text{ex-phon}}|$, whereas, the decrease of dot size leads to delocalize the wave functions of both electron and hole, in turn, decreases $|E_{\text{ex-phon}}|$. However, the size dependence of exciton-LO-phonon coupling is a complicated problem to be investigated.

In this letter, we qualitatively compared the PL spectra of various ZnO particle sizes and quantitatively deduced the weighting of exciton-LO-phonon coupling strength. We finally obtained the reduction of exciton-LO phonon interaction with decreasing ZnO particle sizes.

ZnO QDs and powders were synthesized by sol-gel method, which was published previously. Stoichiometric zinc acetate dihydrate [99.5% Zn(OAc)$_2$·2H$_2$O, Riedel-deHaen] was dissolved into diethylene glycol (99.5% DEG cethylenediamine-tetra-aceticacid). The resultant solution was centrifuged at 3000 rpm for 30 min and a transparent solution was then obtained containing dispersed single crystalline ZnO QDs. Finally, the supernatant was dropped on a Si(001) substrate with native oxide and dried at 150 °C. The samples of 5.3, 7.4, and 12 nm in diameter were obtained for further studies. ZnO micrometer size powders were synthesized by Zn(OAc)$_2$·2H$_2$O and methanol. The concentration of Zn$^{2+}$ was 0.35 mol/l. The sol was annealed in a furnace at 900 °C under air atmosphere for 1 h, and then slowly cooled to room temperature. The PL measurement was made using a 40 mW He–Cd laser at a wavelength of 325 nm and the emission light was dispersed by a TRIAX-320 spectrometer and detected by an UV-sensitive photomultiplier tube. A closed cycle refrigerator was used to set the temperature anywhere between 13 and 300 K.

Figure 1(a) shows the PL spectrum of different ZnO sizes at 13 K. The spectrum of ZnO powders consists of the free exciton (FX) and the donor-bound exciton (D$^0$X) emission peaks along with three obvious LO-phonon replicas. The FX emission of ZnO powders is 3.77 eV which behaves as ZnO bulk. The energy shift (dash line) from 3.377 to 3.475 eV due to quantum confinement effect can be observed. The full width at half maximum which increases as the dot size decreases may be caused by the contribution of surface-optical phonon, surface-bound acceptor exciton complexes, and size distribution. Accordingly, we observed that LO-phonon replicas are obvious in ZnO powders but are unapparent in other QD samples. Duke and Mahan interpreted that the intensities of LO-phonon replicas depend strongly on their exciton-phonon coupling strengths.

Figure 1(b) displays the temperature-dependent PL of 7.4 nm QDs; it reveals only a single band for $T=13 \sim 300$ K. Due to small binding energy of D$^0$X, it will be ionized as $T>$100 K, so we can easily attribute the single band to the FX emission. We also find that the peak energy difference of FX between 13 and 300 K is $\sim$25 meV, which is smaller than 65 meV of the ZnO powders. It is known that the main contribution to the energy shift is the Fröhlich interaction, a result of Coulomb interaction. From the temperature-dependent PL, we can obtain the exciton binding energy ($E_b$) from the following relation.

\[ E_b = \frac{2}{3} \epsilon_0 \epsilon_r \frac{e^4 a}{2m^*} \]

\[ \frac{E_b}{k_B T} = \frac{2}{3} \frac{e^2}{\epsilon_0 \epsilon_r a} \]

where $\epsilon_0$ is the vacuum permittivity, $\epsilon_r$ the relative dielectric constant of the medium, $e$ the elementary charge, $m^*$ the effective mass of the exciton, $a$ the exciton Bohr radius, and $k_B$ the Boltzmann constant. The exciton Bohr radius can be estimated by $a_B = \frac{\hbar^2}{\epsilon_0 \epsilon_r \epsilon a m^*}$, where $\hbar$ is the reduced Planck constant. The exciton binding energy is then given by $E_b = \frac{2}{3} \frac{e^2}{\epsilon_0 \epsilon_r a}$. The exciton Bohr radius can be estimated by $a_B = \frac{\hbar^2}{\epsilon_0 \epsilon_r \epsilon a m^*}$, where $\hbar$ is the reduced Planck constant. The exciton binding energy is then given by $E_b = \frac{2}{3} \frac{e^2}{\epsilon_0 \epsilon_r a}$.
coupling strength of the optical phonon with energy $\omega_{\text{LO}}$ involved in RRS and PL is the one having energy of $71\text{–}72$ meV. We therefore take only one of the summation terms with $h\omega=72$ meV into account to discuss the exciton-LO phonon coupling. Then the $\alpha_0$ represents the weighting of exciton-LO-phonon coupling. Although the LO-phonon energy depends on the size of QD, from our fitting result even for 5.3 nm QD, the phonon energy shift is less than 1 meV, it is insufficient ($<44\%$) to change $\alpha_0$. We plotted the fitting results $\alpha_0=0.59, 0.40, 0.21,$ and 0.19 for powders, 12 nm, 7.4 nm, and 5.3 nm QDs, respectively, in Fig. 3. These results are consistent with the observations of PL spectra, weakening coupling strength of exciton-LO phonon as decreasing the particle sizes.

The increasing $E_b$ gives an indication for reduction of exciton-LO phonon interaction. The enhancement of $E_b$ or Coulomb potential indicates a reduction of $\alpha_b$. It makes the exciton less polar capable for efficiently interacting with LO-phonon through the Fröhlich interaction. To find out the relation between $\alpha_b$ and $\alpha_0$, we calculated $\alpha_b$ from our PL spectra including the FX emission energy and $E_b$ for different dot sizes based on the weak confinement model as follows:\textsuperscript{19}

$$E_b(R) = E_g + \frac{\pi^2 \hbar^2}{2 e R^2 \mu} - \frac{1.8 e^2}{4 \pi \varepsilon_0 R^3},$$

and $\alpha_b^2 = h^2/(2 \mu_0 c^2 E_b).$\textsuperscript{20} where $E_b(R)$ is the measured FX emission energy plus $E_b$, $E_g=3.43$ eV is the band gap energy.
of bulk ZnO, e is the charge of electron, $\hbar$ is Planck’s constant divided by 2$\pi$, $R$ is the particle radius, $\mu^*$ is the reduced mass of exciton, $\varepsilon=3.7$ is the relative permittivity, and $\varepsilon_0$ is the permittivity of free space. The calculated exciton Bohr radii $a_B \ QD$ for 5.3, 7.4, and 12 nm QDs are 0.977, 1.038, and 1.328 nm. The ratios of $a_B \ QD$ to the exciton Bohr radius for bulk ZnO of $a_B \ bulk=2.34$ nm are 0.42, 0.46, and 0.57, respectively, which agree well with 0.42, 0.49, and 0.59 obtained by Senger and Bajaj.

Figure 4 shows similar trends of $a_0 \ QD/a_0 \ powders$ and $a_B \ QD/a_B \ powders$ against the dot size. It shows that the exciton formation is attained by Coulomb interaction; as the particle sizes decrease, the quantum confinement effect causes increase of $E_b$ and decrease of $a_B$. The electric dipole, which is proportional to the distance of electron-hole pair, is then reduced. The exciton formation thus becomes less polar, reducing the coupling strength with the polar lattice via the Fröhlich interaction. Consequently, we demonstrated that the reduction of exciton-LO phonon interaction occurs in ZnO-QD system.

We presented temperature-dependent PL of different sizes of ZnO particles. The unobvious LO-phonon replicas of FX were observed when the ZnO particle sizes were under 12 nm in diameter. The FX emission energy difference of 13–300 K decreases as the particle size decreases. The increasing exciton $E_b$ with the decreasing quantum dot size can be obtained from temperature-dependent PL. From the temperature-dependent change of FX emission energy, the exciton-LO phonon coupling strength reduces as the particle size decreases. This is consistent with reducing LO-phonon replica in PL spectra and our previous RRS results. The reduced $a_B$ with particle size obtained from $E_b$ and PL spectrum confirms that the exciton becomes less polar, in turn, reducing the Fröhlich interaction; and the exciton-LO phonon interaction is reduced with decreasing ZnO QDs.

This work was partially supported by the National Science Council Taiwan under Contract No. NSC 96-2628-M-009-001-MY3.