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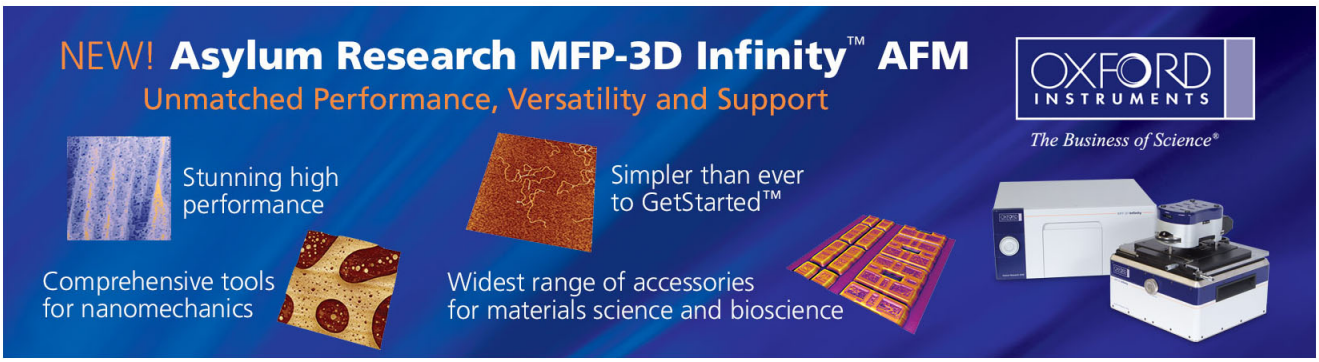

Reducing exciton-longitudinal-optical phonon interaction with shrinking ZnO quantum dots

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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 ($E_b \sim 60$ meV).[1] 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,[2] optically pumped lasers,[3] and other electronic devices.[4] Although a large number of researches on II-VI QDs and III-V QDs have been published,[5,6] 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.*[7] 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,[8] the resonant Raman scattering (RRS) of various ZnO QD sizes reveals that decrease of I_{2LO}/I_{1LO} with decreasing particle sizes gives an evidence for the reduction of exciton-LO phonon interaction with decreasing QD size. Chang and Lin [9] theoretically reported that the exciton LO-phonon interaction energy $|E_{ex\text{-}ph}|$ 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 $|E_{ex\text{-}ph}|$; whereas, the decrease of dot size leads to delocalize the wave functions of both electron and hole, in turn, decreases $|E_{ex\text{-}ph}|$. 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.[10,11] Stoichiometric zinc acetate dihydrate [99.5% $Zn(OAc)_2 \cdot 2H_2O$, 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 $Zn(OAc)_2 \cdot 2H_2O$ 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^0X) emission peaks along with three obvious LO-phonon replicas.[11] The FX emission of ZnO powders is 3.377 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,[12] surface-bound acceptor exciton complexes,[13] 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.[14]

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^0X, 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 ~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,[15] a result of Coulomb interaction. From the temperature-dependent PL, we can obtain the exciton binding energy (E_b) from the following relation:[16]

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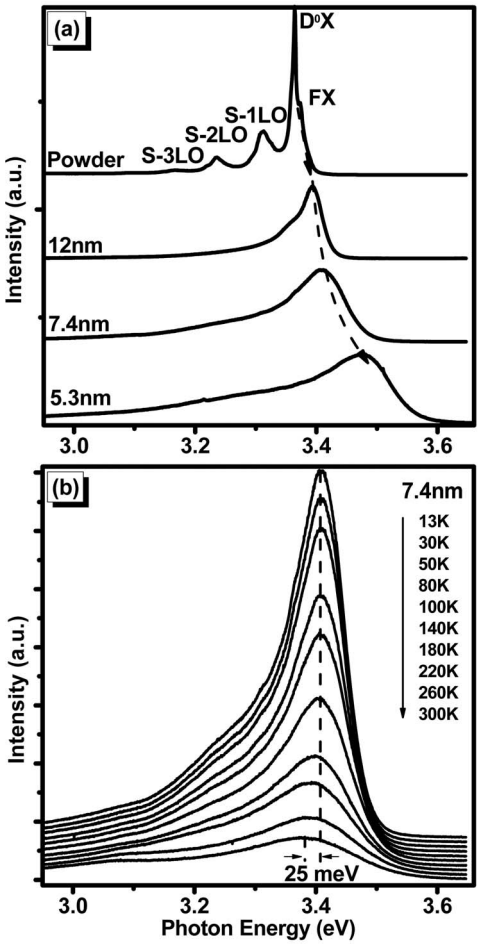

FIG. 1. (a) PL spectra of different ZnO particle sizes at 13 K. The dashed line indicates the FX peak energy shift. (b) Temperature-dependent PL spectra of 7.4 nm of ZnO QDs in the range of 13–300 K. The dashed lines marked the peak energies of 13 and 300 K. Their energy difference is 25 meV.

$$I(T) = \frac{I(0)}{1 + A\exp(-E_b/k_BT)}, \tag{1}$$

where $I(T)$ is the integrated intensity of the peak at a specific temperature, $I(0)$ is the integrated intensity at absolute zero, A is a constant, and k_B is Boltzmann's constant. The fitting results are shown in Fig. 2; E_b of the ZnO powder is 60 meV, which is close to that of ZnO Bulk. We obtained E_b=67, 87, and 132 meV, respectively, for 12, 7.4, and 5.3 nm QDs. The decreasing particle size would raise the electron-hole interaction as a result of the compressing boundary to cause increasing Coulomb energy. Therefore, the binding energy increases as the particle size decreases.

In order to quantitatively investigate the relation between the quantum confinement size and the exciton-LO phonon interaction, we introduced the temperature-dependent exciton energy[17]

$$E_{ex}(T) = E_{ex}(0) - \sum_i \frac{\alpha_{0i}}{\exp(\hbar\omega/k_BT) - 1}, \tag{2}$$

where $E_{ex}(T)$ is the exciton energy at a specific temperature T, $E_{ex}(0)$ is the exciton energy at 0 K, and α_{0i} represents the coupling strength of the optical phonon with energy $\hbar\omega_i$. As our previous RRS (Ref. 8) and PL results, the most promising LO phonon involve in RRS and PL is the one having

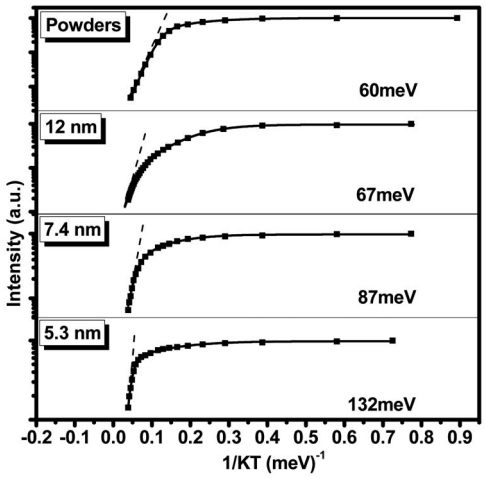

FIG. 2. The FX integral intensity as a function of the inverse temperature from 13 to 300 K for different ZnO particle sizes. Squares represent experimental data, while solid lines are the theoretical fitting.

energy of 71–72 meV. We therefore take only one of the summation terms with $\hbar\omega$=72 meV into account to discuss the exciton-LO phonon coupling. Then the α_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 α_0. We plotted the fitting results α_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 a_B. It makes the exciton less polar capable for efficiently interacting with LO-phonon through the Fröhlich interaction.[18] To find out the relation between a_B and α_0, we calculated a_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:[19]

$$E_g(R) \approx E_g + \frac{\pi^2\hbar^2}{2eR^2\mu^*} - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 R}, \tag{3}$$

and ${a_B}^2=\hbar^2/(2\mu^* E_b)$,[20] where $E_g(R)$ is the measured FX emission energy plus E_b, E_g=3.43 eV is the band gap energy

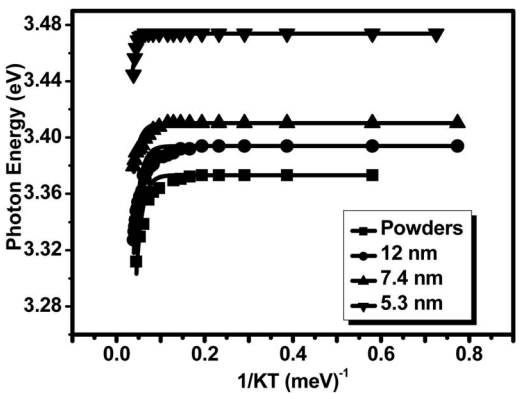

FIG. 3. Experimental and calculated (solid line) exciton energies plotted against inverse temperature for different ZnO particle sizes.

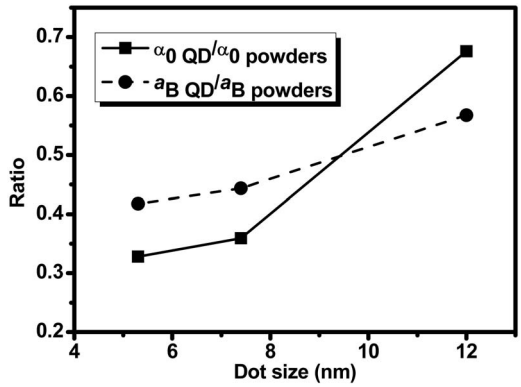

FIG. 4. The relation of $\alpha_{0\ \mathrm{QD}}/\alpha_{0\ \mathrm{powders}}$ and $a_{B\ \mathrm{QD}}/a_{B\ \mathrm{powders}}$ with different dot sizes.

of bulk ZnO, e is the charge of electron, $\hbar$ is Planck's constant divided by 2π, R is the particle radius, μ^* is the reduced mass of exciton, $\varepsilon=3.7$ is the relative permittivity,[21] and ε_0 is the permittivity of free space. The calculated exciton Bohr radii $a_{B\ \mathrm{QD}}$ for 5.3, 7.4, and 12 nm QDs are 0.977, 1.038, and 1.328 nm. The ratios of $a_{B\ \mathrm{QD}}$ to the exciton Bohr radius for bulk ZnO of $a_{B\ \mathrm{bulk}}=2.34$ 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.[22]

Figure 4 shows similar trends of $\alpha_{0\ \mathrm{QD}}/\alpha_{0\ \mathrm{powders}}$ and $a_{B\ \mathrm{QD}}/a_{B\ \mathrm{bulk}}$ 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.[18] 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.[8] 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.

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