行政院國家科學委員會專題研究計畫 期中進度報告

雷射技術及時析光譜研究奈米光電材料與結構之研究(第 1 年)
期中進度報告(精簡版)

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行政院國家科學委員會補助專題研究計畫□ 成 果 報 告 □X 期中進度報告

光電奈米材料與結構中激子之控制(1/3)

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計畫主持人：謝文峰

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中　　華　　民　　國 97 年 5 月 22 日

行政院國家科學委員會專題研究計畫成果報告

光電奈米材料與結構中激子之控制(3/1)

Toward Control of Excitons in Photonic Nano-materials and Structures (3/1)

計畫編號：NSC 96-2628-M-009 -001 -MY3
執行期限：96 年 8 月 1 日至 97 年 7 月 31 日
主持人：謝文峰教授　　國立交通大學光電工程學系

一、中文摘要

我們發現激子與縱聲子交互作用隨著氧化鋅量子點縮小導致其激子半徑變小而降低。從變溫PL光譜可觀察到較不明顯的自由激子—縱聲子複製發光和較小溫度變化的自由激子發光譜之平移，以及自由激子發光強度的分析，我們確定Fröhlich交互作用之降低乃是由於量子侷限效應使得量子點中之激子半徑縮小導致激子極化降低，以至於激子與晶格震盪之庫倫作用降低。

關鍵詞：聲子散射、溶膠—凝膠法、II-VI 族半導體、寬能隙半導體、氧化鋅、激子、螢光、量子侷限。

Abstract

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.

Keywords: Phonon scattering; Sol–gel; II-VI semiconductor, wide band gap, ZnO, exciton, quantum confinement.

二、緣由與目的

During the last decade, zinc oxide (ZnO) has received much attention because of its wide band gap and large binding energy (E_b ~ 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 report, 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.

三、研究方法與步驟

ZnO QDs and powders were synthesized by sol-gel method, which was published previously.[10,11] Stoichiometric zinc acetate dihydrate (99.5% Zn_OAc_2·2H2O, 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·$2H_2O$ 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.

四、結果與討論

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 -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] $I(T)=\frac{I(0)}{1+A\exp(-E_b/k_BT)}$, 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] $E_{ex}(T)=E_{ex}(0)-\sum_i \frac{\alpha_{0i}}{\exp(\hbar\omega_i/k_BT)-1}$, 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 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] $E_g(R)\approx E_g+\frac{\pi^2\hbar^2}{2eR^{2\mu^*}}-\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 R}$, 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 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, ε=3.7 is the relative permittivity,[21] and ε_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.[22] We found similar trends of $\alpha_{0\text{-QD}}/\alpha_{0\text{-powders}}$ and $a_{B\text{-QD}}/a_B$ 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.

五、結論

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 *Eb* 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.

六、自我評估

本年度計畫中我們進行兩部分光電物理之研究，分別為氧化(鎂)鋅薄膜與量子點之成長與光電性質研究和光子晶體波導之理論探討等。我們利用雷射濺鍍與 sol-gel 法成功地成長氧化(鎂)鋅薄膜與量子點等。成長之樣品我們分別研究，激子—聲子之交互作用、螢光、受激輻射與雷射現象、拉曼散射等等。在光子晶體波導研究方面，我們以緊束縛原理首次成功地解釋光子晶體波導的偶合與不偶合現象。這一年來共發表 12 篇光電材料相關的 SCI 論文，即雷射動力學相關研究 SCI 論文計 3 篇，成果還算不錯。

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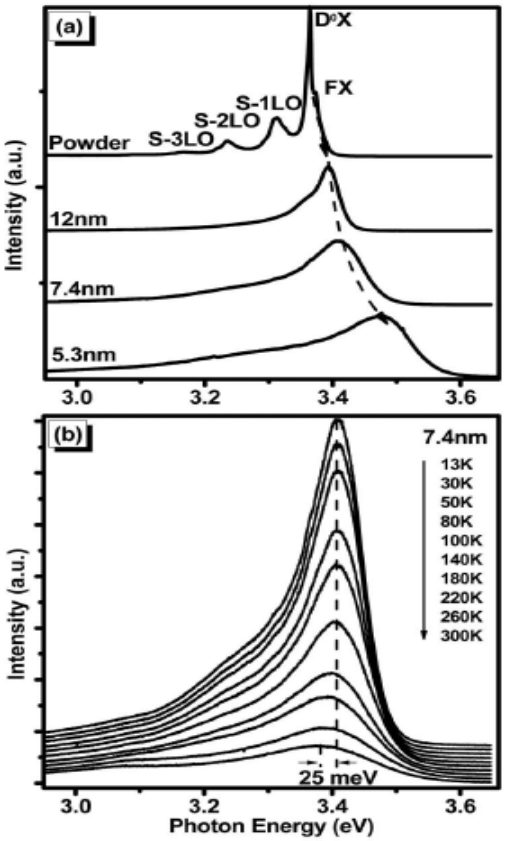

FIG. 1. (a) PL spectra of different ZnO particle sizes at 13 K. The dashed line indicates the FX peak energy shift. (b) Temperature-dependent PL spectra of 7.4 nm of ZnO QDs in the range of 13–300 K. The dashed lines marked the peak energies of 13 and 300 K. Their energy difference is 25 meV.

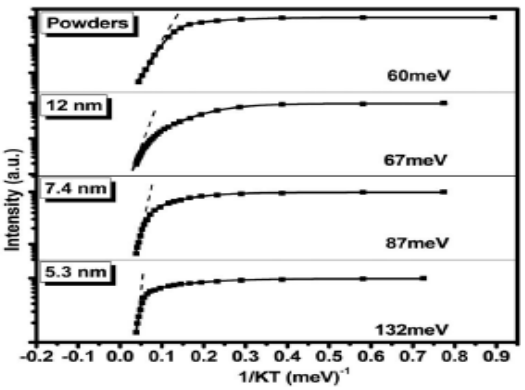

FIG. 2. The FX integral intensity as a function of the inverse temperature from 13 to 300 K for different ZnO particle sizes. Squares represent experimental data, while solid lines are the theoretical fitting.

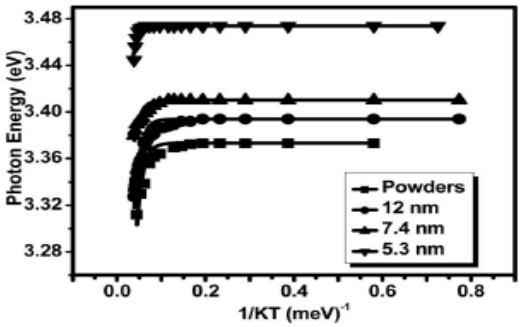

FIG. 3. Experimental and calculated (solid line) exciton energies plotted against inverse temperature for different ZnO particle sizes.