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Temperature-dependent photoluminescence study of InP/ZnS quantum dots

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Abstract
This paper reports on the temperature-dependent photoluminescence of InP/ZnS quantum dots under 532 nm excitation, which is above the InP transition energy but well below that of ZnS. The overall photoluminescence spectra show two spectral components. The higher-energy one (named X) is assigned to originate from the excitonic transition; while the low-energy spectral component (named I) is normally interpreted as resulting from lattice imperfections in the crystalline structure of InP/ZnS quantum dots (QDs). Peak positions of both the X and I emissions vary similarly with increasing temperature and the same as the InP bandgap narrowing with temperature. In the temperature range from 15 to 80 K, the ratio of the integrated intensity from the X and the I emissions decreases gradually and then this ratio increases fast at temperatures higher than 80 K. This could result from a population of charge carriers in the lattice imperfection states at a temperature below 80 K to increase the I emission but then with these charge carriers being released to contribute to the X emission.

1. Introduction

Semiconductor quantum dots (QDs) or nanocrystals (NCs) have been intensively studied over the past 20 years. The main concerns in semiconductor QDs or NCs are their large surface and quantum confinement that give rise to interesting optical properties. Since QD average sizes are comparable to the Bohr radius of the exciton in bulk materials, the energy state of electrons and holes are quantized [1]. Consequently, the emission wavelength varies as a function of QD size. Due to their unique optical properties, they are of considerable interest for both fundamental research and technological applications. Among them, mainly II–VI semiconductor QDs, such as CdSe and CdTe, have been studied due to their strong luminescence in the visible spectral range [2–6]. Compared to the II–VI QDs, III–V compounds are less toxic because they are composed of elements that are more environmentally friendly than Cd, Se or Te. InP is a typical III–V semiconductor material that has a direct band gap with a bandgap energy of 1.27 eV. Within the past decade, InP QDs have been synthesized using various methods [7–12]. Like II–VI semiconductors, InP QDs clearly exhibit the quantum size effect and size-dependent optical characteristics. High-quality InP QDs can be used as fluorescent probes in biological labeling, as light emitters or absorbers in opto-electronic devices, such as light emitting diodes and solar cells. As-prepared InP NCs generally show weak luminescence because of the existence of non-radiative channels originating from surface states. After appropriate surface treatments, e.g. with HF etching [13] or by overgrowth with a ZnS shell [10–17], InP NCs can become highly luminescent materials. Using Zn in the syntheses of InP QDs and making the ZnS shell, depending on the methods used, we have prepared two structures, namely the InP/ZnS

real core/shell QDs and the In(Zn)P/ZnS alloy QDs. They both emit strong luminescence in the green-to-red region with a high luminescence quantum yield (QY). In the InP/ZnS real core/shell QDs, photoluminescence (PL) spectra from the InP QD core and the ZnS shell were clearly observed [18], while for the In(Zn)P/ZnS alloy QDs, only a strong luminescence from In(Zn)P QDs was observed but not from the ZnS shell [19, 20]. In a close-packed In(Zn)P/ZnS sample, we observed not only an emission peak originating from the excitonic transition but also that resulting from lattice imperfections in the crystalline structure [19].

In this paper, we highlight the results on the temperature-dependent PL of semiconductor close-packed InP/ZnS real core/shell QDs. The 532 nm laser line was chosen as the excitation source to be sure that only the InP QDs are excited and not the ZnS shell. Deconvolution of the overall PL spectra shows two spectral components peaking around 2.06 eV (named the X band) and 1.8 eV (named the I band), which are, respectively, interpreted as resulting from the excitonic transition and from lattice imperfections in the crystalline structure of InP/ZnS QDs. Peak positions of both the X and I emissions vary similarly with increasing temperature and the same as the temperature-dependence of the InP bandgap energy. The ratio of the integrated PL intensity from the X and I emission bands has been analysed as a function of temperature, showing its different changes with temperature, related to the charge carrier populations in the I states.

2. Experimental

InP/ZnS core/shell QDs were prepared by a two-step in one-pot method. 0.1 mmol of indium acetate In(Ac)$_3$ were mixed with 0.3 mmol of myristic acid and 6.8 g of 1-octadecene (ODE) in a three-neck flask. The mixture was heated to 100–120 °C to obtain an optically clear solution. The flask was degassed for 3 h and backfilled with N$_2$ gas. Then, it was heated to 290 °C. The P precursor was provided in the form of PH$_3$ gas, generated by the reaction of 1.2 mmol Zn$_3$P$_2$ powder with 5 ml 4 M H$_2$SO$_4$ in a separate flask. Both flasks were connected. PH$_3$ gas was bubbled into the reaction flask and reacted with an indium precursor to form InP NCs. The color of the reaction mixture quickly changed from colorless to deep red during 2 min of reaction. The ZnS shell was made by the slow addition of air-stable ZnS precursors (0.4 mmol zinc stearate ZnSt$_2$ and 0.1 mmol zinc ethylxanthate Zn(EX)$_2$ in mixed solvent of ODE, toluene and dimethylformamide DMF) to the crude InP core NCs at 275 °C in 10 min. The high quality of the synthesized InP/ZnS alloy QDs was confirmed by x-ray diffraction and their UV-vis (not shown in this paper).

In the PL measurements, the 532 nm laser line, which is above the InP transition energy but well below that of ZnS, was used as the excitation source. The PL signals were dispersed by using a 0.55 m grating monochromator (Horiba iHR550) and then detected by a thermoelectrically cooled Si-CCD camera (Synapse). To deconvolute the overall spectra into reasonable components, the best curve fits were performed based on the assumption that each band has a Lorentz shape.
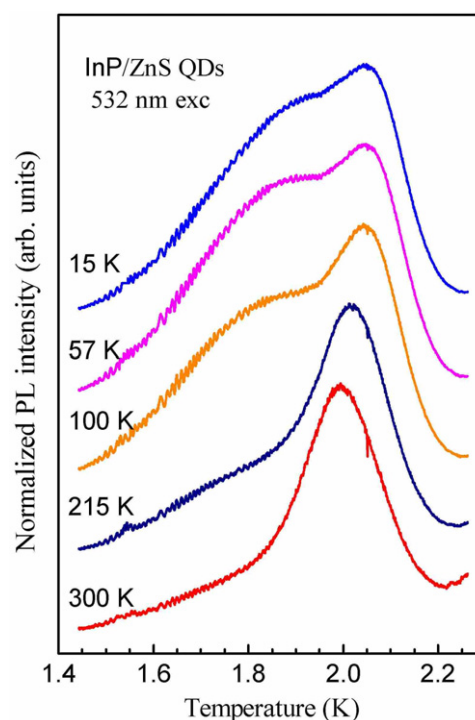

Figure 1. PL spectra of InP/ZnS QDs as a function of temperature.

3. Results and discussion

As-synthesized InP/ZnS core/shell NCs emit rather strong photoluminescence. In most of the samples they were synthesized by using the two-step in one-pot method, but in some samples the emission from ZnS was visible along with the strong luminescence of InP QDs. In some samples we did not observe the emission from the ZnS shell besides the one from InP QDs, even under 266 nm excitation, possibly meaning that the ZnS shell is too thin to emit its proper emission. Figure 1 shows the normalized PL spectra of InP/ZnS core/shell QDs under 532 nm laser line excitation at various temperatures from 15 to 300 K. Emission of InP/ZnS core/shell QDs under 532 nm excitation is attributed to originate from the excitonic transition and from lattice imperfections of the InP QDs only. For these QDs, in addition to the narrow peak at around 2.06 eV (the X band), a shoulder at lower energy around 1.8 eV (the I band) is visible. Generally, such broad emission bands, namely I in this case, located at the energy lower than the excitonic peak, are related to lattice imperfections in the crystalline structure, as observed also in CdTe QDs [21]. The experiment shows that the temperature-dependence of each spectral band mentioned above (X and I) is different. This relates to the activation energy of each one correspondingly. It is clearly seen that the I emission was strong at low temperature but is thermally quenched to become only a very weak shoulder at room temperature.

To study in more detail the evolution between these X and I emission bands, we have analyzed the data from the temperature-dependent PL spectra. Figure 2 presents the integrated intensity ratio of the X and I emission band (hereafter called the X/I ratio) from the InP/ZnS core/shell QDs as a function of temperature under 532 nm excitation.
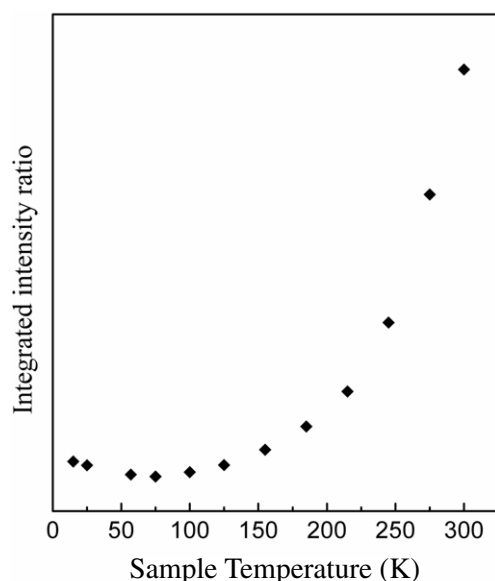
Figure 2. Temperature-dependence of the X/I ratio from InP/ZnS QDs under 532 nm excitation.

Figure 3. Peak positions of the X and I spectral components from InP/ZnS QDs as a function of temperature. Dots are experimental data. Lines are the fits with equation (1).

As mentioned already in the experimental part, the choice of 532 nm excitation is important to avoid any interference of the ZnS shell in the InP QD emission. In the temperature range from 15 to 80 K, the X/I ratio decreases gradually and then this ratio increases fast at temperatures higher than 100 K. It is quite possible that there exist traps with the activation energy of 8 meV (corresponding to the kT at 80 K). These traps are populated with photo-generated carriers at temperatures below 80 K and consequently induce the pronounced I emission and reduce the X emission. As a result, the X/I ratio is small in this temperature range. At temperatures above 100 K, the trapped carriers are released contributing to the X emission, to quickly increase the X/I ratio, as presented in the figure.

In general, any electronic transition could relate more or less to the lattice vibrations. Therefore, we wonder if in a very small assembly of atoms forming a nanocrystal the contribution of the microfield induced by lattice vibrations is still taking place, giving rise to the red-shift of emissions with increasing temperature. The microfield originating from lattice vibration in the bulk crystal is normally taken place of 80% to induce the bandgap narrowing with increasing temperature, while the 20% left is the contribution of thermally induced dilatation of the lattice constants [22, 23]. Figure 3 gives the answer to this query; it presents the peak positions of the X and I spectral components as a function of temperature. The peak positions of both the X and I emissions vary similarly with temperature, namely red-shift gradually with an increase in the temperature. The red-shift of all two peak positions was determined to be about 60 meV with an increase in the temperature from 15 to 300 K, similar to the values obtained from other materials, e.g. ZnO and ZnS, and this could be the same as the energy shift of the InP bandgap. Thus, some characteristics normally taken place in the bulk materials could happen even in a very small assembly of atoms in a nanocrystal, e.g. the effect of bandgap narrowing with temperature and the emission from donor–acceptor pair recombination [24].
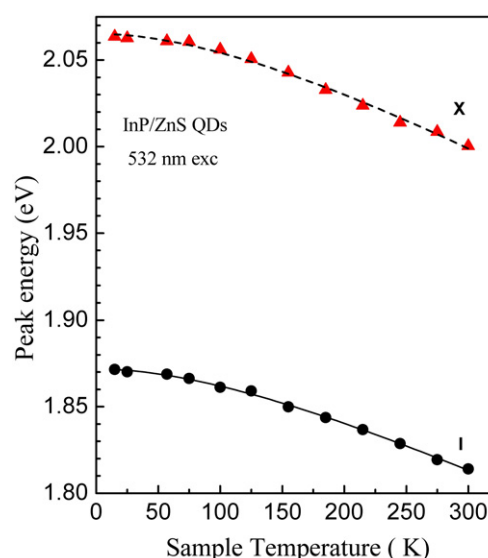
The variations in the X and I emissions with temperature are fitted to Varshni's equation,

$$E(T) = E(0) - \frac{\alpha T^2}{\beta + T}, \qquad (1)$$

where $E(T)$ is the transition energy at temperature T, $E(0)$ is the transition energy at 0 K and α, β are Varshni's coefficients. For easier identification of each peak position, we have named the peak position of X as xc1 and I as xc2, respectively. The best fit has yielded the values $E_1(0) = 2.065$ eV, $\alpha_1 = 3.8 \times 10^{-4}$ eV K^{-1}, $\beta_1 = 282$ K; and the values $E_2(0) = 1.872$ eV, $\alpha_2 = 4.5 \times 10^{-4}$ eV K^{-1}, $\beta_2 = 311$.

4. Conclusion

In conclusion, we have studied the temperature-dependence of photoluminescence from InP/ZnS QDs by using 532 nm light as the excitation source. This choice of the excitation wavelength/energy is important to excite the InP QDs but not the ZnS shell. The overall photoluminescence spectra show two spectral components, namely the X and I band, which originated from the excitonic transition and lattice imperfections in the crystalline structure, respectively. Peak positions of both the X and I emissions vary similarly with increasing temperature and the same as the InP bandgap narrowing with temperature. This means that even with a very small assembly of atoms to form nanocrystals, the temperature-dependence of energy levels takes place the same as in the bulk, meaning that the contribution of the microfield induced by lattice vibrations in very small assemblies of atoms. In the temperature range from 15 to 80 K, the integrated PL intensity ratio of the X and I emissions decreases gradually and then increases quickly with temperatures higher than 80 K, probably resulting from a population of charge carriers in the lattice imperfection states at temperatures below 80 K. At temperatures higher than 80 K, these trapped carriers were released to contribute to the X emission.

Acknowledgment

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