Polaron Effects in Quantum Dots

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Based on the polaron effect, we have provided a theoretical explanation for the photoluminescence (PL) spectra of a single InP/GaInP quantum dot, the characteristic features of which are a set of equally separated peaks and large linewidth. The phonon band required for our theory has recently been discovered as the disorder activated longitudinal acoustic band around 20 meV. Our theoretical predictions on the temperature dependence and the light polarization dependence of the PL spectra have initiated new experiments, which have confirmed our theory.

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As characteristic features of a confined zero dimensional system, electron energies in a quantum dot (QD) are well-separated discrete levels. Then, the light emitted from a QD should be extremely sharp, which is important for optical devices. From a sample with high QD density, fabricated with the standard Stranski-Krastanow mechanism, the measured finite linewidth of photoluminescence (PL) was attributed to the variation of QD sizes. Recently, PL spectra of a single InP/GaInP QD have been obtained [1] from fully developed dots with a well-defined shape. The base area is 45×60 nm^2 with the elongation in the [110] direction and the height is typically between 12 and 18 nm. Regardless from which QD in a sample the spectrum is taken, in every PL spectrum one observes sets of peaks. In each set the peaks are equally separated by an energy of about 20 meV. While the emission spectra from different dots are quite similar with respect to energy spacing between the peaks, the intensity ratio of the peaks varies. Furthermore, every sharp PL peak has a finite linewidth of about 2 meV, which is substantially larger than the thermal energy k_BT for the experimental temperature $T = 5$ K. One typical experimental measurement is shown in Fig. 1, where the PL spectrum exhibits two sets of peaks. The main set has three peaks marked as *A*, *B*, and *C*, and the second set of three weak peaks is shifted from the main set by about 12 meV. The proposed interpretation in terms of hot carriers luminescence process [1] has failed to explain the ratio of peak intensities and the 2 meV linewidth.

Using a six band Luttinger Hamiltonian and taking into account the observed geometry of the dot, the electronic structure of a strained InP/InGaP QD, calculated recently by Pryor *et al.* [2], yields only two PL peaks, corresponding to peaks *A* and *B* in Fig. 1. As the QD height increases from 12 to 18 nm, the peak separation drops from 18 to 13 meV, which is much smaller than the observed 20 meV in all dots. Above the energy of the higher peak, the electronic structure predicts absolutely no PL intensity. Pryor *et al.* [2] have also realized that in a highly symmetric QD, other observed peaks in Fig. 1 cannot be produced by an asymmetry effect. Furthermore, the electronic structure cannot explain the observed 2 meV PL linewidth. Consequently, Fig. 1 can hardly be explained by electronic structure effects.

In this Letter we present a theoretical understanding of the measured PL spectra in terms of electron-phonon interaction and demonstrate the polaron effect as the origin of the interesting features shown in Fig. 1. Our theory predicts a characteristic temperature dependence of the intensity of each PL peak in any PL spectrum, regardless from which QD the spectrum is taken. New experiments motivated by our theory have confirmed this prediction. Our theory has been further checked by the latest experiment on polarization dependence of the PL spectrum. The 20 meV phonon mode which is crucial to our theory has been discovered in a recent Raman experiment [3]: a disorder

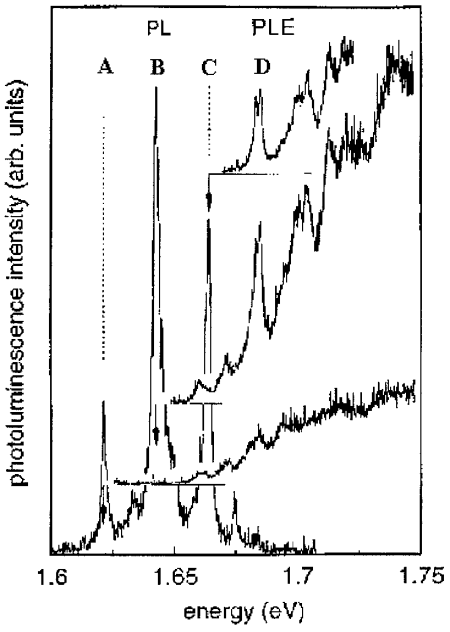

FIG. 1. PL and photoluminescence excitation (PLE) spectrum of a single InP/GaInP QD (from Ref. [1] with permission of the authors).

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activated longitudinal acoustic (DALA) band with energy around 20 meV appears in the measured vibration spectrum of GaInP layer on which InP QDs are grown epitaxially.

To illustrate unambiguously the essential physics of the polaron effect, we will extend the theory of the electron-phonon interaction for localized electronic states in the bulk [4] to the electron-hole system in a quantum dot [5] within the one mode approximation. As in the theory of multiphonon transitions [4] the local vibration is characterized by an effective mass M, a frequency ω, and a configuration coordinate x. From the measured peak separation in Fig. 1 which is equal to the measured energy of the DALA band [3], we have $\hbar\omega = 20$ meV. Since the phonon dispersion has been ignored in our model, in this Letter we will not calculate the PL linewidth but instead will provide a satisfactory explanation of its origin.

Within the adiabatic approximation, the adiabatic potential $U_1(x) = M\omega^2 x^2/2$ describes the local vibration in the absence of an electron-hole pair. Before switching on the electron-phonon interaction, the presence of an electron-hole pair with energy ε_0 raises $U_1(x)$ to $U_2(x) = \varepsilon_0 + U_1(x)$. Then, due to the electron-phonon interaction, ε_0 becomes x-dependent $\varepsilon(x)$. In its simplest form $\varepsilon(x) = \varepsilon_0 - \alpha x$, $\varepsilon(x)$ is linear in x, where the constant α is proportional to the electron-phonon coupling strength. Hence, the adiabatic potential is further modified to

$$\begin{aligned}\tilde{U}_2(x) &= \varepsilon_0 - \alpha x + M\omega^2 x^2/2 \\ &= \varepsilon_0 + (M\omega^2 x^2/2)(x - x_0)^2 - M\omega^2 x_0^2/2 ,\end{aligned} \tag{1}$$

where $x_0 = \alpha/M\omega^2$ is the equilibrium position of shifted oscillator, and $\Delta\varepsilon_{\rm pol} \equiv M\omega^2 x_0^2/2$ is the polaron energy. All these energy profiles are shown in Fig. 2. The energy difference $\varepsilon_{\rm opt} = U_2(0) - U_1(0)$ is the photoexcitation energy of the electron-hole pair, and the separation $\varepsilon_T = \tilde{U}_2(x_0) - U_1(0)$ is its thermal excitation energy. Their difference $\Delta\varepsilon_{\rm pol} = \varepsilon_{\rm opt} - \varepsilon_T$ gives the polaron shift.

The values of α, ω, and M depend on the material and geometrical constants of the QD through the DALA eigenmode. Unfortunately, there exists no concrete theoretical study on a DALA band, although it has been detected in numerous disordered materials in the last 20 years. Because of this, we do not have information to include the nonadiabatic effects in the model. As will be shown below, for our simple model, these three parameters α, ω, and M will be combined into a single variable ζ_0. While $\hbar\omega = 20$ meV, ζ_0 will be fixed by fitting the measured intensity ratio of PL peaks.

In the low temperature limit, only the ground vibration level is populated. Hence, the radiative recombination of electron-hole pair is due to the transition from the ground vibration state $\Psi_0(x - x_0)$ in the potential $\tilde{U}_2(x)$ to the nth vibration state $\Psi_n(x)$ in the potential $U_1(x)$.

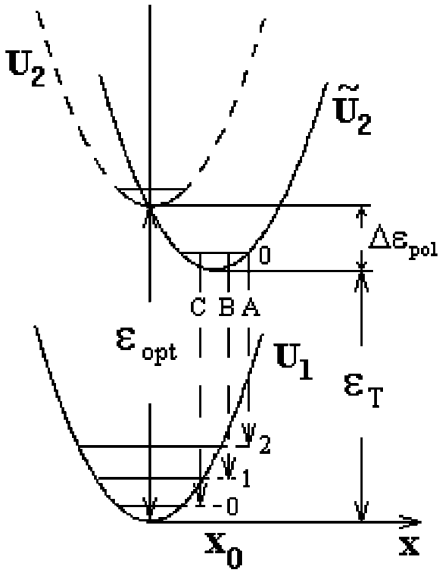

FIG. 2. A schematic plot of various energies which appear in the theoretical model. The transitions A, B, and C give the three corresponding peaks in Fig. 1. See text for details.

The so produced luminescence spectrum will consist of a series of peaks equally separated by the phonon energy $\hbar\omega$. We follow the Condon approximation to neglect the dependence of electron wave functions on the configuration coordinate. Then, the optical transition probability $W_{0,n}$ between $\Psi_0(x - x_0)$ and $\Psi_n(x)$ is

$$W_{0,n} = I_n \left(\sum_{n=0}^{\infty} I_n \right)^{-1} , \tag{2}$$

where $I_n = |\int_{-\infty}^{\infty} dx\, \Psi_n^*(x)\Psi_0(x - x_0)|^2$. Since $\Psi_n(x)$ is the nth eigenfunction of the harmonic oscillator potential $U_1(x) = M\omega^2 x^2/2$, analytical results can be readily derived. In terms of the dimensionless coordinate variable $\zeta_0 \equiv x_0\sqrt{M\omega/\hbar}$, we obtain $\Delta\varepsilon_{\rm pol} = (\hbar\omega/2)\zeta_0^2$, and

$$I_n = \frac{\zeta_0^{2n}}{2^n n!} \exp(-\zeta_0^2/2) . \tag{3}$$

Thus, the relative peak intensities in a PL spectrum, given by Eq. (3), are determined by the parameter ζ_0, the value of which depends on the electron-phonon coupling in the QD. We should point out that $\zeta_0^2/2$ is just the Huang-Rhys parameter which appears in the theory of multiphonon transition. Equations (2) and (3) indicate that the pattern of distribution of the normalized peak values in a PL spectrum is rather sensitive to the value of ζ_0^2. As an example, two sets of calculated PL peak intensities are shown in Fig. 3 for $\zeta_0^2 = 1.5$ (a) and $\zeta_0^2 = 2.5$ (b). Hence, the value of ζ_0 will be determined by fitting the measured PL spectrum as demonstrated below.

The increase of n in Fig. 3 corresponds to the decrease of photon energy in Fig. 1. We notice that in the PL spectrum shown in Fig. 1, the peak B in the main set

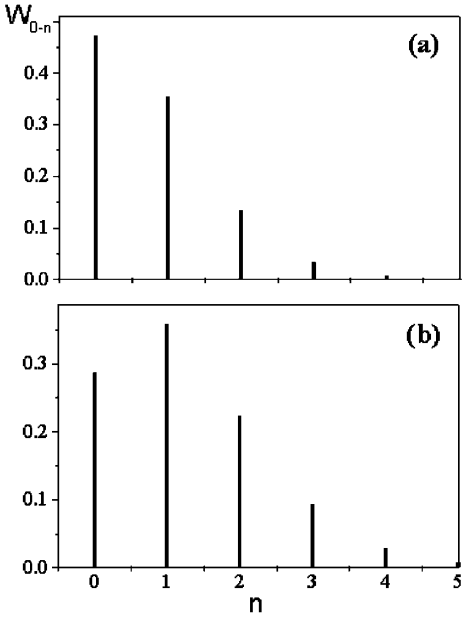

FIG. 3. Two calculated distribution patterns of PL peak intensities for $\zeta_0^2 = 1.5$ (a) and $\zeta_0^2 = 2.5$ (b).

overlaps with the middle peak in the second set of peaks with much weaker intensity. After deconvolution, the pattern of relative peak intensities of the main set is very similar to the one shown in Fig. 3(b). Hence, the QD parameter is so determined as $\zeta_0^2 = 2.5$. From Fig. 2 it is clear that a set of equally separated peaks in the PL spectrum will shift uniformly in energy if ϵ_{opt} and/or $\Delta\epsilon_{\text{pol}}$ vary. Since different electron-hole pair excitations give different values of ϵ_{opt} and $\Delta\epsilon_{\text{pol}}$, more than one set of equally separated peaks may appear in a single PL spectrum. However, peak separations in all sets are the same because they all originate from the same DALA band. For a given set, since all peaks correspond to the radiative recombination of the same electron hole pair, their intensities should have the same time dependence which is determined by the decay of the electron hole pair. This is indeed the experimental observation [1] that all three peaks *A*, *B*, and *C* in Fig. 1 have the same value of time constant 0.6–0.7 ns. Our theoretical calculation has then explained the measured PL spectra in terms of polaron effects. In the measured phonon spectrum of Ref. [3], the DALA band has a width of about 2 meV. Hence, if we introduce a phonon dispersion of about 2 meV and then perform a complete theoretical analysis accordingly, the δ peaks in Fig. 2 will be broadened and the linewidth will be about 2 meV. Such detailed calculation will not be presented in this Letter.

In order to check whether our theory of polaron effects is correct, we have suggested two new experiments to the group who measured the PL spectrum in Fig. 1. The first is the temperature quenching of PL intensity. The temperature dependence of multiphonon assisted nonradiative recombination of electron-hole pairs can be readily calculated with our theory. The nonradiative recombination process is determined by the thermally stimulated tunneling. Within the semiclassical approximation the probability $1/\tau_{\text{ph}}(T)$ for this process is given by [4]

$$\frac{1}{\tau_{\text{ph}}(T)} = \frac{1}{\tau}\exp[-\phi(T)],$$
$$\phi(T) = \left[-\frac{\hbar\omega}{2k_BT} + \ln\frac{1+\sqrt{1+\xi^2}}{\xi} - \sqrt{1+\xi^2} + \xi\cosh\frac{\hbar\omega}{2k_BT}\right]\frac{\varepsilon_T}{\hbar\omega}, \quad (4)$$

where $\xi = \Delta\varepsilon_{\text{pol}}/[\varepsilon_T \sinh(\hbar\omega/2k_BT)]$.

Since the probability of radiative recombination is insensitive to temperature, while the probability of nonradiative recombination is enhanced rapidly with increasing temperature, the PL intensity $I(T)$ will be reduced when the temperature is raised. Let τ_{rad} be the lifetime of the radiative process. Using a reference temperature T_0 (usually the lowest experimental temperature), we define $\gamma = \tau_{\text{rad}}/\tau_{\text{ph}}(T_0)$. For a given peak in the PL spectrum, in terms of its reference intensity $I(T_0)$, the PL intensity at higher temperature T is readily obtained as

$$I(T) = \left[\frac{1+\gamma}{1+\gamma\exp[\phi(T_0)-\phi(T)]}\right]I(T_0). \quad (5)$$

The intensity ratio $I(T)/I(T_0)$ depends only weakly on $\Delta\varepsilon_{\text{pol}}$ as compared to its dependence on the phonon energy $\hbar\omega$. Hence, Eq. (5) should represent the characteristic temperature dependence of all peaks in all PL spectra taken from all QDs in one sample.

Using the same samples from which the PL spectra were taken earlier, new experiments have been performed [6] to measure the temperature dependence of the PL intensity of a number of peaks in different QDs, in a temperature range from 5 to 85 K. The reference temperature is then set at $T_0 = 5$ K. The measured values of relative intensity, expressed in the form $\ln[I(T)/I(5\text{ K})]$, are plotted in Fig. 4 with different symbols for different PL peaks. To calculate $\ln[I(T)/I(5\text{ K})]$ from Eq. (5), we need to know the values of ε_T and γ. From the position of peak *C* in Fig. 1, we obtain $\varepsilon_T = 1.665$ eV. Treating γ as a fitting parameter, our theoretical result calculated with $\gamma = 0.075$ is shown in Fig. 4 as the solid curve. The very small value of γ is expected because at very low temperature 5 K, the electron-hole recombination is almost entirely radiative. This experimental confirmation of our theory clearly indicates that the polaron effects play a very important role in the optical properties of a single InP/GaInP QD.

It is important to point out that if one believes that the observed interesting features in PL spectra are caused by the electronic structure effects, and uses the electronic structure of Ref. [2] to calculate the temperature

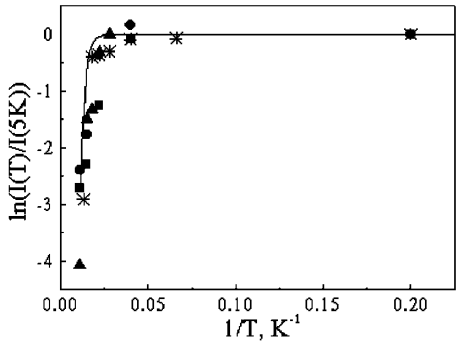

FIG. 4. Temperature dependence of individual peak intensity $I(T)/I(5\text{ K})$ in a PL spectrum of a single InP/GaInP QD. Different symbols are for different peaks, and the data are collected from more than one QD (Ref. [6]). The solid curve is the theoretical result calculated from Eq. (5).

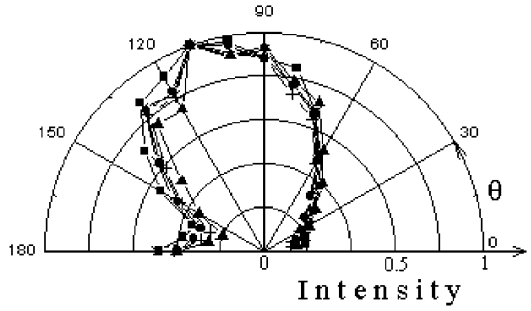

FIG. 5. Polarization dependence of the normalized intensity (with respect to the intensity at $\theta = 110°$) in a PL spectrum of a single InP/GaInP QD, with different symbols for different peaks (Ref. [6]).

dependence of PL peak intensity, the so-obtained result differs drastically from the measured data at the qualitative level.

It was conjectured in Ref. [2], in connection to its electronic structure calculation, that besides peaks *A* and *B*, all other PL peaks in Fig. 1 are due to the QD asymmetry. We then suggested the second experiment to measure the polarization dependence of the PL intensity, which is determined by the symmetry properties of the electron-hole pair wave function, but not by the eigenfunction $\Psi_n(x)$ of the harmonic oscillator potential. If that conjectured in Ref. [2] is correct, different PL peaks of a given QD cannot have the same polarization dependence. If our polaron model is correct, then all equally separated PL peaks in the same set measured from a given QD should have the same polarization dependence.

The suggested experiment has also been performed [6] on the same samples from which the PL spectra were measured earlier. The polarization direction of the incident light is fixed, and the PL spectrum is taken for a given polarization direction of the emitted light. Let θ be the angle between the two polarization directions and $I(\theta)$ the corresponding PL intensity. The data from a QD exhibit a maximum intensity for all PL peaks at $\theta = 110°$. The normalized intensities $I(\theta)/I(110°)$, measured along the radial direction, are plotted in Fig. 5 as functions of θ, where each symbol represents a PL peak. It is clear that all data taken from different PL peaks in a given QD have exactly the same symmetry. Consequently, the prediction based on the polaron effects is consistent with the experimental results shown in Fig. 5, while the conjecture based on the electronic structure effects contradicts the observation.

The PLE spectra were measured together with the PL spectra, as shown in Fig. 1. Although the 20 meV PLE line separation also appears in PLE spectra in the energy region around 1.7 eV, at the moment we have no intention to interpret these extremely complicated PLE spectra for the following reason. According to the electronic energy level structure of a strained InP/InGaP QD [2], the energy level spacing is about 10 meV for electrons and about 2 meV for holes, which are comparable to the electron-phonon interaction energy. Thus, there are sophisticated dynamical and nonadiabatic processes embedded in the PLE spectra. In this connection, we should also mention that perhaps similar processes are required to explain the effect of external electric field on the PL spectrum [7].

While our simple polaron model explains very well the PL spectra of a single InP/GaInP QD, there exists no work on the formation of such polaron.

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