Excitonic transitions in Be-doped GaAs/AlAs multiple quantum well*

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A series of GaAs/AlAs multiple-quantum wells doped with Be is grown by molecular beam epitaxy. The photoluminescence spectra are measured at 4, 20, 40, 80, 120, and 200 K, respectively. The recombination transition emission of heavy-hole and light-hole free excitons is clearly observed and the transition energies are measured with different quantum well widths. In addition, a theoretical model of excitonic states in the quantum wells is used, in which the symmetry of the component of the exciton wave function representing the relative motion is allowed to vary between the two- and three-dimensional limits. Then, within the effective mass and envelope function approximation, the recombination transition energies of the heavy- and light-hole excitons in GaAs/AlAs multiple-quantum wells are calculated each as a function of quantum well width by the shooting method and variational principle with two variational parameters. The results show that the excitons are neither 2D nor 3D like, but are in between in character and that the theoretical calculation is in good agreement with the experimental results.

Keywords: GaAs/GaAlAs mulitiple quantum wells, heavy- and light-hole excitons, photoluminescence spectra, variational calculation

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1. Introduction

Quasi-two-dimensional semiconductor-based quantum well and superlattice structures have extensively been investigated because of their potential applications in compact Terahertz emitters, cascade lasers, small-size detectors, etc.[1–5] A characteristic feature of the optical spectra of quantum well and superlattice systems at low temperatures is the occurrence of excitons. The exciton is often treated as a 'two-body' combination involving an electron and a hole between which there is Coulombic interaction. In a three-dimensional (3D) crystal of semiconductor bulk material the envelope function $\phi_{\rm r}$ describing the relative motion of excitons between an electron and a hole in the ground state has the following form:

$$\phi_{\rm r} = \exp\left(-\frac{r}{\lambda}\right), \tag{1}$$

where $r^2 = (x_{\rm e} - x_{\rm h})^2 + (y_{\rm e} - y_{\rm h})^2 + (z_{\rm e} - z_{\rm h})^2$ and λ is the Bohr radius of the exciton. It is clear that the function $\phi_{\rm r}$ has the same 3D symmetry as the Hamiltonian describing the relative motion term. The scenario also holds true for a two-dimensional (2D) exciton confined to a plane, with the function $\phi_{\rm r}$ now having the form

$$\phi_{\rm r} = \exp\left(-\frac{r_\perp}{\lambda}\right), \tag{2}$$

where $r_\perp^2 = (x_{\rm e} - x_{\rm h})^2 + (y_{\rm e} - y_{\rm h})^2$.

In a quantum well or superlattice structure, the problem is complicated by the quantum-well confined potential existing along the z-direction. Therefore, the exciton in a quantum confined system is neither 2D nor 3D like. However, in the majority of theoretical calculations of the transition and binding energies of the excitons in the literature, the shape of wave function representing the electron-hole relative motion is usually chosen as either the 2D[6–8] or 3D exciton[9,10] given by Eqs. (2) and (1), respectively. Choosing function $\phi_{\rm r}$, the exciton problem can then be solved to various degrees of sophistication. In addition, the exciton in an anisotropic or confined system is also studied by the model of fractional-dimensional space,[11–14] in which the anisotropic or confined system can be treated as an isotropic system in the effective fractional-dimensional space, and excitonic bound-state energies and wave functions are obtained by solving the simple hydrogenic Schrödinger equation in the fractional-dimensional space.

In this paper, the envelope function $\phi_{\rm r}$ describing the electron-hole relative motion in the ground state is taken as the intermediate between the 2D and 3D limit, which has the following form:

$$\phi_{\rm r} = \exp\left(-\frac{r'}{\lambda}\right), \tag{3}$$

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where $r'^2 = (x_e - x_h)^2 + (y_e - y_h)^2 + \zeta^2(z_e - z_h)^2 = r_\perp^2 + \zeta^2 a^2$ and both ζ and λ are used as variational parameters, which are systematically varied in the numerical calculation so as to minimize the energy of the exciton. This fractional-dimensional choice for ϕ_r is rarely found in the literature. Then, within the effective mass and envelope function approximation, the transition recombination energies of the heavy- and light-hole excitons in GaAs/AlAs multiple-quantum wells are calculated each as a function of the quantum well width by the shooting method and variational principle with two variational parameters. Experimentally, we measure photoluminescence (PL) spectra at various temperatures for a series of GaAs/AlAs multiple quantum wells with Be δ-doping at the well center together with a single epilayer of GaAs with uniform Be doping (GaAs:Be). The transition recombination energies of the heavy- and light-hole excitons are measured, respectively for the samples with different quantum well sizes. Finally, the calculating results are compared with the experimental results.

2. Experiment and results

A series of GaAs/AlAs multiple-quantum wells was grown on semi-insulating (100) GaAs substrates by molecular-beam epitaxy with Be acceptors δ-doped at the quantum-well center. The growth of the layers was performed under the exact stoichiometric condition using the technique of low-temperature growth, which ensures high-quality optical materials even at relatively low growth temperatures. Under these conditions, the quantum-well structures were grown at 550 °C or 540 °C without interruptions at the quantum well interfaces, which ensured negligible diffusion of the Be δ layers. Prior to the growth of the multiple-quantum wells, a GaAs buffer layer of 300 nm was grown. Each of the multiple-quantum well structures investigated contained an identical 5-nm-wide AlAs barrier, while each GaAs well layer was δ doped at the well center with Be acceptor atoms. The doping level, doping mode and main characteristics of each of the samples are summarized in Table 1. The sample 7 is a 5-μm-thick single GaAs:Be epilayer with uniform Be doping, which is used as a reference with the quantum well width being infinite and Be acceptors being under no quantum confinement. For the sample 5, the beryllium acceptors were uniformly doped in the 2-nm central region of a 20-nm GaAs quantum-well layer instead of the δ-doping at the well center. Furthermore, in comparison with other samples, sample 6 has a special structure, where an $Al_{0.3}Ga_{0.7}As$ barrier was grown at the central 2-nm region of a 10-nm well layer and doped uniformly with Be acceptors, i.e., each of the 10-nm quantum wells is divided again into two 4-nm-wide quantum wells by the 2-nm-wide $Al_{0.3}Ga_{0.7}As$ barrier.

Table 1. Characteristics of the samples: the repeated period, quantum-well width (L_w), Be-doped concentration (P), doping mode and growth temperature (T) of the epitaxial layer.

Samples	Periods	L_w/nm	P/cm^{-2}	Doping modes	T/°C
1	400	3	2×10^{10}	δ-doped at well center	550
2	200	10	5×10^{10}	δ-doped at well center	550
3	50	15	2.5×10^{12}	δ-doped at well center	540
4	40	20	2.5×10^{12}	δ-doped at well center	540
5	100	20	5×10^{10}	uniformly doped in the 2-nm central region of well	550
6	200	10	5×10^{10}	uniformly doped in 2-nm $Al_{0.3}Ga_{0.7}As$ barrier	550
7	a single 5-μm-thick epilayer (GaAs:Be)		2×10^{16}	uniformly doped in the bulk	550

Photoluminescence experiments were performed from liquid helium to room temperature using a Renishaw RM1000 Raman microscope. The samples were mounted on a cold finger of a continuous flow Helium cryostat. The optical excitation for PL experiments was provided by an argon-ion laser (514.5 nm). The laser beam was focused onto a sample, and the light reflected from the sample was collected and entered into a spectrometer for analysis. The excitation power was typically 5 mW.

The PL spectra with above-band-gap excitation have been measured at the various temperatures for the samples in Table 1. Figure 1 shows the PL spectra at 4, 20, 40, 80, 120, and 200 K for sample 5. Three peaks are clearly resolved at 4 K, with energy positions located at (1.5247±0.0002), (1.5287±0.0002), and (1.5337±0.0002) eV, respectively. The first labeled Be^0X at (1.5247±0.0002) eV is the strongest peak and originates from the recombination of excitons bound to the neutral beryllium acceptor. The second strongest peak at (1.5287±0.0002) eV is attributed to the transition of a free heavy-hole exciton $X_{CB1-HH1}$. The energy separation between the $X_{CB1-HH1}$ and Be^0X is 4 meV, which is the energy required to remove an exciton from the Be^0X complex. The third strongest peak, $X_{CB1-LH1}$, located at (1.5337±0.0002) eV arises from the recombination emission of free light-hole excitons. In addition, on the low energy side of the Be^0X there is an even weaker peak in intensity than the $X_{CB1-LH1}$,

$X_{CB1-HH1}$, and Be^0X, which is attributed to the free-to-bound recombination eBe^0 between an electron of the $n = 1$ quantized confined level and a hole bound to a Be acceptor at the center of the GaAs well. At 40 K below, the intensities of the $X_{CB1-HH1}$ and $X_{CB1-LH1}$ peak are both enhanced as the measuring temperature rises, while both positions slightly shift towards the low energy. When the temperature reaches up to 40 K, the intensity of the $X_{CB1-HH1}$ exceeds that of Be^0X. This is because the kinetic energy of free excitons increases with temperatures rising, which makes it hard that the free excitons are bound by acceptors to become bound excitons, and which gives rise to a reduction of the number of bound excitons. However, for temperatures above 80 K, as the measuring temperature further increases, neither Be^0X nor eBe^0 is detectable, with the energy positions of $X_{CB1-LH1}$ and $X_{CB1-HH1}$ observably shifting towards the low energy. This is attributed to the monotonic reduction of the band gap of GaAs bulk material with the temperatures rising. Furthermore, compared with sample 4 which has the same well width as sample 5 but is δ-doped with Be acceptors at the well center, sample 5 has slightly greater transition energies of the heavy- and light-hole excitons for sample 5, specifically, the $X_{CB1-HH1}$ and $X_{CB1-LH1}$ are (1.5285 ± 0.0002) eV and (1.5335 ± 0.0002) eV at 20 K for sample 5 respectively, while they are (1.5269 ± 0.0002) eV and (1.5314 ± 0.0002) eV, respectively, for sample 4.[15] Therefore, the differences in transition energies at 20 K between both samples are 1.6 meV and 2.1 meV for the $X_{CB1-HH1}$ and $X_{CB1-LH1}$, respectively. The doping sheet concentration of sample 4 with Be acceptors δ-doped at the well center is roughly two orders of magnitude higher than that of sample 5. Subsequently, the ions of δ-doped Be acceptors will form a spike potential in the quantum-well center, which forces the energy level of the ground state of electrons to be lowered with respect to the conduction band bottom, while the energy levels of the heavy- and light-holes shift towards the valence-band top. Consequently, the recombination emission energies of free excitons for sample 4 are less than those of sample 5.

Figure 2 illustrates the PL spectra of sample 6 at different temperatures. In comparison with Fig. 1, however, only two emitting peaks are observed at temperature 4 K, which are the $X_{CB1-HH1}$ and Be^0X located at (1.6659±0.0002) eV and (1.6577±0.0002) eV, respectively. The Be^0X is a very weak shoulder peak, but neither $X_{CB1-LH1}$ nor eBe^0 can be resolved clearly. The quantum well size of sample 6 is 4 nm much narrower than that of sample 5, thus the electrons and holes in the GaAs quantum-well layer are confined more strongly by the quantum-well potential, resulting in the fact that the energy levels of the ground state and excited states of electrons holes rise relatively. Therefore, this makes it difficult that the heavy-hole excitons are captured by Be acceptors and that the light-hole excitons are formed by Coulomb interactions between an electron and a hole.[16]

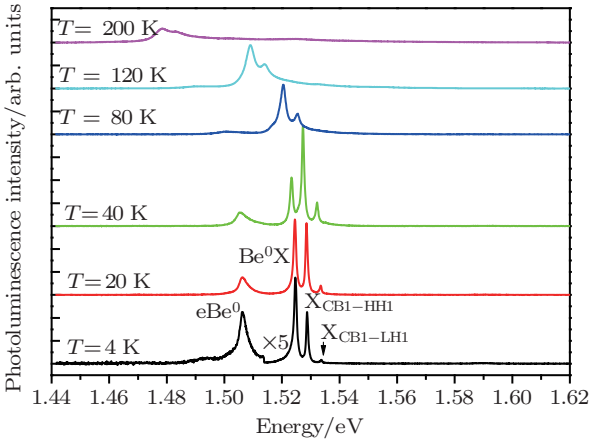


Fig. 1. (color online) Series of PL spectra for sample 5 at 4, 20, 40, 80, 120, and 200 K, showing the $X_{CB1-LH1}$, $X_{CB1-HH1}$, Be^0X, and eBe^0 peaks.

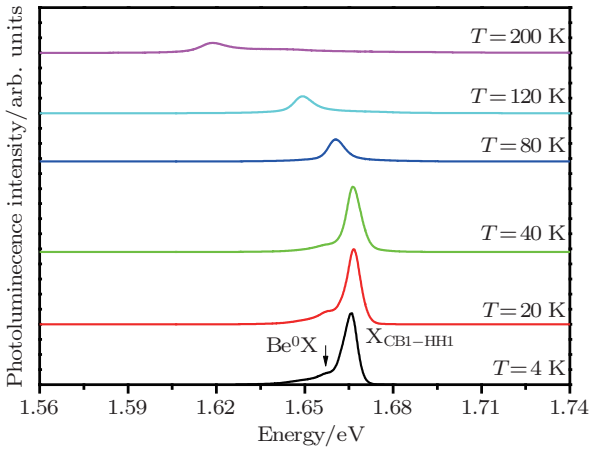


Fig. 2. (color online) Series of PL spectra for sample 6 at temperatures of 4, 20, 40, 80, 120, and 200 K, showing the $X_{CB1-HH1}$ and Be^0X peaks.

3. Calculation and discussion

3.1. Theoretical model

Under the effective mass and envelope function approximations, for an exciton in the GaAs/AlAs quantum well, the Hamiltonian representing the interacting two-body electron-hole complex can be considered as the sum of three terms

$$H = H_e + H_h + H_{e-h}, \tag{4}$$

where H_e and H_h are the one-particle Hamiltonians appropriate to the conduction and valence bands, respectively, of the GaAs/AlAs quantum well. The one-particle Hamiltonians are written as

$$H_e = -\frac{\hbar^2}{2m_e^*}\frac{\partial^2}{\partial z^2} + V_{CB}(z),$$
$$H_h = -\frac{\hbar^2}{2m_h^*}\frac{\partial^2}{\partial z^2} + V_{VB}(z). \tag{5}$$

The third term H_{e-h} on the right-hand side of Eq. (4) represents the electron-hole interaction, which is composed of two

terms. One of these terms corresponds to the kinetic energy of the relative motion of the electron and hole in the x–y plane (perpendicular to the growth axis), while the other represents the Columbic potential energy, i.e.,

$$H_{\mathrm{e-h}} = \frac{p_\perp^2}{2\mu_\perp} - \frac{\mathrm{e}^2}{4\pi\varepsilon r}, \tag{6}$$

where $p_\perp$ is the quantum mechanical momentum operator for the in-plane component of the relative motion, and $\mu_\perp$, $\mu_\perp^{-1} = m_{\mathrm{e}}^{*-1} + m_{\mathrm{h}}^{*-1}$, the reduced mass of the electron–hole pair.

$$p_\perp^2 = -\hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \tag{7}$$

and r is simply the electron-hole separation, given by

$$r^2 = (x_{\mathrm{e}} - x_{\mathrm{h}})^2 + (y_{\mathrm{e}} - y_{\mathrm{h}})^2 + (z_{\mathrm{e}} - z_{\mathrm{h}})^2. \tag{8}$$

The problem consists in finding the eigenfunctions Ψ and eigenvalues of the Schrödinger equation:

$$H\Psi = E\Psi. \tag{9}$$

The two-body exciton wave function Ψ is taken as a product of three factors as follows:

$$\Psi = \psi_{\mathrm{e}}(z_{\mathrm{e}})\psi_{\mathrm{h}}(z_{\mathrm{h}})\psi_{\mathrm{r}}, \tag{10}$$

where ψ_{r} is a variational wave function employed to minimize the total energy E of the system. The other two factors, $\psi_{\mathrm{e}}(z_{\mathrm{e}})$ and $\psi_{\mathrm{h}}(z_{\mathrm{h}})$, are simply the eigenfunctions of the one-particle Hamiltonians of the GaAs/AlAs quantum well:

$$\begin{aligned} H_{\mathrm{e}}\psi_{\mathrm{e}}(z_{\mathrm{e}}) &= E_{\mathrm{e}}\psi_{\mathrm{e}}(z_{\mathrm{e}}), \\ H_{\mathrm{h}}\psi_{\mathrm{h}}(z_{\mathrm{h}}) &= E_{\mathrm{h}}\psi_{\mathrm{h}}(z_{\mathrm{h}}). \end{aligned} \tag{11}$$

One of the main advantages of this formalism is that it is independent of the forms of the one-particle Hamiltonians H_{e} and H_{h}, and indeed calculations can be performed on any system in which the standard electron and hole wave functions can be calculated.[15,17,18]

Multiplying Eq. (9) on the left by Ψ and integrating over all space, then the total exciton energy follows simply as the expectation value:

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{12}$$

The wave function ψ_{r} representing the electron–hole relative motion in the ground state is chosen to be a function of a hydrogenic atom, given by

$$\psi_{\mathrm{r}} = \exp\left(-\frac{r'}{\lambda}\right), \tag{13}$$

where the Bohr radius λ will be used as a parameter and systematically varied in order to minimize the total energy E of the system. A variable symmetry-type relative motion is chosen as

$$r'^2 = (x_{\mathrm{e}} - x_{\mathrm{h}})^2 + (y_{\mathrm{e}} - y_{\mathrm{h}})^2 + \zeta^2(z_{\mathrm{e}} - z_{\mathrm{h}})^2. \tag{14}$$

The second variational parameter, ζ, allows the exciton to be assumed to have any shape of wave function in a fractional-dimensional space. Traditionally, the case with $\zeta = 0$ has become known as the two-dimensional exciton,[7,8] and $\zeta = 1$, as a three-dimensional exciton.[9,10] The cases where ζ is allowed to take values other than 0 and 1 are rarely found in the literature.

3.2. Results and discussion

Using Eq. (11), the one-particle electron and hole eigenstates, $\psi_{\mathrm{e}}(z_{\mathrm{e}})$ and $\psi_{\mathrm{h}}(z_{\mathrm{h}})$, are calculated numerically by the shooting method, respectively, and then substituted into Eq. (12) together with ψ_{r}. The parameters of λ and ζ are systematically varied in order to minimize the total energy E of the system. In the numerical calculation, the effective mass values of the electron and hole, m_{e}^* and m_{h}^*, are taken as the typical values for bulk GaAs, i.e., $0.067m_0$ and $0.62m_0$, respectively, where m_0 is the rest mass of an electron in the free space. The relative dielectric permittivity ε_{r} is set to be 13.18.

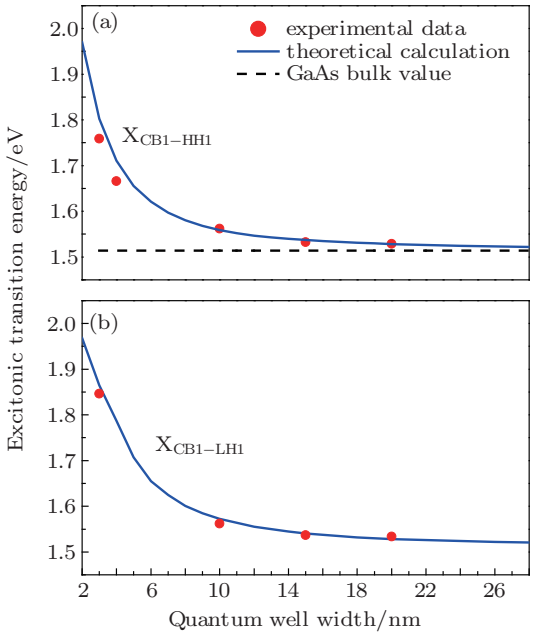


Fig. 3. (color online) Plots of exciton transition energy versus quantum well width in a 5-period GaAs/5 nm AlAs multiple quantum wells for (a) heavy-hole excitons and (b) light-hole excitons.

Figure 3 displays the variational calculation results of recombination transition energies of heavy-hole $X_{CB1-HH1}$ and light-hole $X_{CB1-LH1}$ excitons, respectively, as a function of the quantum well width for the 5-period GaAs/5 nm AlAs multiple quantum wells, in which a finite structure resembles an infinite structure. It is clearly seen from Fig. 3 that the transition energies of both heavy-hole and light-hole excitons fall monotonically as the quantum well width increases, and are in good

agreement with measured data of photoluminescence spectra. In addition, for the heavy-hole exciton $X_{CB1-HH1}$ at 4.2 K, the transition energy tends smoothly towards the value of bulk GaAs:Be, i.e., (1.5142±0.0002) eV.[19] However, the reason is that the quantum confined effect on the electrons or holes in the wells becomes weak as the well thickness increases. Theoretically, when the well width goes to infinity, the quantum confined effect on the carriers in the wells tends toward zero, where the carriers are the same as those in the GaAs bulk.

Figure 4 shows the variations of parameter ζ in the variational calculation for the heavy and light-hole excitons, $X_{CB1-HH1}$ and $X_{CB1-LH1}$, with quantum well width for the 5-period GaAs/5 nm AlAs quantum wells, respectively. It can be seen from Fig. 4 that both of ζ rise as the quantum well thickness increases. Furthermore, the ζ value determines in physical meaning the shape dimensionality of spatial wave functions of excitons. Traditionally, when $\zeta = 0$ and $\zeta = 1$, the excitons correspond to two-dimensional (2D) and three-dimensional (3D) excitons, respectively. However, the variational calculation method used here differs from that employed by He in Refs. [11] and [13] with the model of fractional-dimensional space, in which an anisotropic system in the 3D space can be treated as an isotropic system in the effective fractional-dimensional space, and excitonic bound-state energies and wave functions are obtained by solving the simple hydrogenic Schrödinger equation in the fractional-dimensional space. Then, Kundrotas *et al.* extended the fractional-dimensional approach to analyze transitions of the free-electron-acceptor impurities located at the center of the quantum well, where effective fractional dimensionality, $1 < \alpha < 3$, is determined by experimental results, such as the PL spectra.[12]

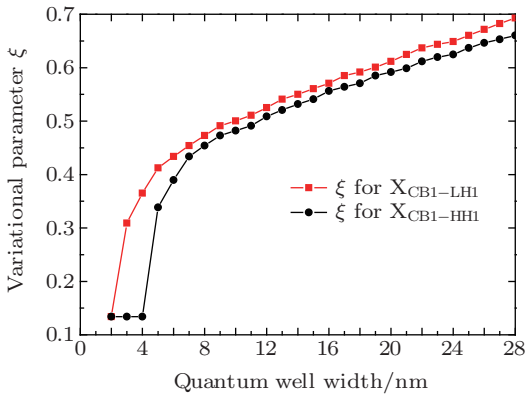


Fig. 4. (color online) Plots of variational parameter ζ versus quantum well depth in the 5-period GaAs/5-nm AlAs quantum wells.

4. Conclusions

We investigate experimentally and theoretically the recombination transition energies of the heavy– and light-hole excitons, $X_{CB1-HH1}$ and $X_{CB1-LH1}$, for a series of GaAs/AlAs multiple quantum wells doped with Be in the wells or in barriers. The PL spectra are measured at the various temperatures, and the recombination emissions of the heavy- and light-hole excitons, $X_{CB1-HH1}$ and $X_{CB1-LH1}$, are clearly observed. The transition energies of the $X_{CB1-HH1}$ and $X_{CB1-LH1}$ is measured experimentally. In addition, within the effective mass and envelope function approximations the recombination transition energies of the heavy- and light-hole excitons are calculated numerically, respectively, as a function of the quantum-well size via the shooting method and variational method involving two variational parameters. The results show that the exciton in the ground state is neither 2D nor 3D like, but is in between in character, and that the theoretical numerical calculation is in good agreement with the result from the measured PL spectra.

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