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Electronic structure and optical properties of zinc-blende GaN quantum dots *

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The energy levels of zinc-blende GaN quantum dots (QDs) are studied within the framework of the effective-mass envelope-function approximation. The dependence of the energy of electron and hole states on the quantum dot (QD) size is presented. The selection rules for optical transitions are given and the oscillator strengths of the dipole-allowed transitions for various QD radii are calculated with the wavefunctions of quantized energy levels. The theoretical absorption spectrum of GaN QDs is in good agreement with the existing experimental result.

Keywords: electronic structure, GaN, quantum dots, optical properties
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1. Introduction

Semiconductor quantum dots (QDs) have attracted much attention not only for a variety of new interesting physical and chemical properties but for their potential applications.[1,2] As the size of QDs is of the order of exciton Bohr radii of their bulk materials, varying the crystal size may result in a considerable shift of their absorption and photoluminescence spectra. This tunable ability opens the opportunity of fabricating QDs based tunable lasers and light-emitting diodes. Another property of QDs, a strong nonlinear optical response, is also attractive in many applications including that as a saturable absorber for mode locking in lasers.[3,4]

Among numerous semiconductors, GaN is an important wide-band-gap semiconductor (3.41eV for hexagonal and 3.2–3.3eV for zinc-blende bulk GaN at room temperature[5]). It has recently received much attention for potential applications as blue-light-emitting and laser diodes, high-speed field-effect transistors, UV photodetectors, and high-temperature electronic devices.[6,7] The appearance of the low-dimensional materials, especially zero-dimensional QDs, would make this perspective of applications more attractive. Nowadays, GaN QDs have been obtained using colloidal chemical method,[5] pulsed laser ablation,[8] and self-organization.[9] Their optical properties have been investigated experimentally, and a shift to higher energy with decreasing QDs size in the optical spectra has been observed.

Electronic structure is important in the understanding of semiconductor materials' physical properties. In the past few years, a series of theoretical method such as tight-binding theory,[10,11] pseudopotential method,[12] as well as effective mass approximation (EMA)[13−15] have been widely used in the calculations of electronic structures of CdS, CdSe, GaAs and so on. As for GaN, Andreev *et al*[16] have presented the electronic structure of GaN/AlN hexagonal QDs, including built-in strain and electric-field effects. However, few articles are involved in zinc-blende GaN QDs which are always obtained using colloidal chemical method.[5] In order to understand the quantum size effects of zinc-blende GaN QDs, a knowledge about electronic structure is in demand.

Among several theoretical methods for electronic structure, the multiple-band effective mass approximation has been successful in describing the absorption,[15] hole burning,[17] and photolumines-

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cence excitation spectra.[18] The assignment of the electronic states based on the EMA provides a foundation for almost every description of electronic structure in QDs.

The following is a theoretical analysis of the electronic structure and absorption spectrum of zinc-blende GaN QDs within the framework of the envelope-function formalism. This paper comprises the following. First, we will consider the energy spectrum and wavefunction of the quantum size levels of the electron and the hole. Then, the selection rules and oscillator strengths for optical transitions between the hole and electron quantized energy levels will be discussed. Finally, the absorption spectra of GaN QDs will be obtained theoretically and compared with the existing experimental result.

2. Calculation method

We consider GaN QDs as spheres with radius a surrounded by an infinitely high potential barrier. The angular and radial parts of the wavefunctions are separable within the framework of EMA. The eigenfunctions of the problem are the product of spherical harmonics(quantum numbers L and L_z), for the angular variation, by radial functions. The condition of vanishing of these radial functions at the surface of the spheres ($r = a$) provides the stationary states of the system. In the treatment of valence bands, we made the so-called spherical approximation, i.e. neglecting the warping between Luttinger parameters: γ_2, γ_3, and $\gamma = (2\gamma_2 + 3\gamma_3)/5$ is used to replace the real value of γ_2.[19]

Due to a wide band gap in GaN, a simple one-band effective mass theory[20] is suitable for the conduction band. Confinement energy of conduction state is $E_{\mathrm{e},nl} = \hbar k_{nl}^2/2m_{\mathrm{e}}a^2$, and wavefunctions are

$$\Psi_{\mathrm{e},nlm}(r) = \sqrt{\frac{2}{a^3}}\frac{\mathrm{j}_l(k_{nl}r)}{\mathrm{j}_{l+1}(k_{nl}a)}\left|l,m\right\rangle\left|S\ \alpha\right\rangle, \qquad (1)$$

where j_l is the spherical Bessel function of the order of l, k_{nl} satisfy the spherical Bessel equation $\mathrm{j}_l(k_{nl}a) = 0$, which denotes the boundary condition. $|l,m\rangle$ are the spherical harmonics $\mathrm{Y}_{l\,m}$, $|S\ \alpha\rangle$ are the Bloch functions at the bottom of the conduction band and α is the projection of the electron spin: $\alpha = \uparrow$ or $\downarrow$.

The calculations of hole energy levels strictly follow that in Ref.[15], in which several analytical expressions are presented within the frame of six-band effective mass Hamiltonian. However, we will adopt a more concise expression for wavefunctions for even states and odd states (notation for wavefunctions accord with those in Ref.[15]). For even states

$$\begin{aligned}\Psi_{FF_z} =& R_{\mathrm{h}1}^{+}(r)\left|L,\frac{3}{2},F,F_z\right\rangle \\ &+ R_{\mathrm{h}2}^{+}(r)\left|L+2,\frac{3}{2},F,F_z\right\rangle \\ &+ R_{\mathrm{s}}^{+}(r)\left|L+2,\frac{1}{2},F,F_z\right\rangle, \end{aligned} \qquad (2)$$

for odd states

$$\begin{aligned}\Psi_{FF_z} =& R_{\mathrm{h}1}^{-}(r)\left|L,\frac{3}{2},F,F_z\right\rangle \\ &+ R_{\mathrm{h}2}^{-}(r)\left|L+2,\frac{3}{2},F,F_z\right\rangle \\ &+ R_{\mathrm{s}}^{-}(r)\left|L,\frac{1}{2},F,F_z\right\rangle, \end{aligned} \qquad (3)$$

where

$$\begin{aligned}&|L,J;F,F_z\rangle \\ &= \sum_{L_z,J_z}\langle L,L_z;J,J_z|F,F_z\rangle|L,L_z\rangle|J,J_z\rangle. \end{aligned} \qquad (4)$$

Function $|L,J;F,F_z\rangle$ is the eigenfunction of total angular momentum in the L-J coupling scheme, L, J, F and F_z are the quantum numbers of the envelope angular momentum, the Bloch angular momentum of the valence band top, the total angular momentum, and the component of the total angular momentum along the z-direction, respectively. $|L,L_z\rangle$ is the spherical harmonic function Y_{LL_z}, $|J,J_z\rangle$ is the Bloch wavefunction, J=3/2, $J_z = \pm 1/2$ for the light holes, J=3/2, $J_z = \pm 3/2$ for the heavy holes, and J=1/2, $J_z = \pm 1/2$ for the spin–orbit splitting states.[21] $\langle L,L_z;J,J_z|\,F,F_z\rangle$ is the Clebsch–Gordan coefficient. In the spherical model, F and F_z are considered to be good quantum numbers, correspondingly including in the basis functions only are those orbital angular momenta L compatible with a given F. The resulting basis set contains at most two functions with $J = 3/2$, $\triangle L = 2$ and one with $J = 1/2$. The radial functions $R_{\mathrm{h}}^{\pm}(r)$ and $R_{\mathrm{s}}^{\pm}(r)$ can be generally expressed by using three spherical Bessel functions $\mathrm{j}_l(k_t r)$ (t=l,h,s),[22] and should satisfy the boundary condition

$$R_{\mathrm{h}}^{\pm}(a) = 0, \quad R_{\mathrm{s}}^{\pm}(a) = 0, \qquad (5)$$

as well as the normalization condition

$$\int \mathrm{d}r r^2 (R_{\mathrm{h}1}^{\pm}(r)^2 + R_{\mathrm{h}2}^{\pm}(r)^2 + R_{\mathrm{s}}^{\pm}(r)^2) = 1. \qquad (6)$$

The absorption spectrum of QDs is constituted by a series of peaks which correspond to the transitions between conduction and valence quantized levels. The oscillator strengths f of these transitions are given by $f = 2\ |\langle \Psi_{\rm h}|\, e\widehat{p}\,|\, \Psi_{\rm e}\rangle|^2 /(m_0\hbar\omega)$, where $|\langle \Psi_{\rm h}|\, e\widehat{p}\,|\, \Psi_{\rm e}\rangle|^2$ is the squared matrix element of the dipole moment between the normalized final and initial states, e is the vector of light polarization, m_0 is the free electron mass, and ω is the transition frequency. For instance, substituting Eqs.(1), (2) and (4) into the squared matrix element of the fundamental transition $1{\rm S}_{3/2} \to 1S_{\rm e}$, we obtain

$$\left|\, \Psi_{1{\rm S}_{3/2}}\,|p|\, \Psi_{1{\rm S}_{\rm e}}\right|^2 = P^2 \left| \int {\rm d}r r^2 R_{\rm e}(r) R^{+}_{\rm h1}(r) \right|^2 . \quad (7)$$

$P^2 = |\langle S\,|p_z|\, Z\rangle|^2$,where S and Z are the Bloch wavefunctions of the conduction-band bottom and valence-band top, respectively; $R_{\rm e}(r)$ is the normalized radial part in Eq.(1), $R^{+}_{\rm h1}(r)$ is determined by Eqs.(5) and (6). Calculation involves all the degenerate states and spin states. Because of the orthonormality of spherical harmonic functions $\langle l\ m\,|LL_z\,\rangle = \delta_{lL}\delta_{mL_z}$, the allowed interband transitions only involve initial and final states which possess common L contributions. Hence, transitions $n{\rm S}_{3/2} \longrightarrow k{\rm S}_{\rm e}$, $n{\rm P}_{3/2} \longrightarrow k{\rm P}_{\rm e}$, etc., with $\Delta l = 0$ and $n{\rm S}_{3/2} \longrightarrow k{\rm D}_{\rm e}$, etc., with $\Delta l = 2$ are dipole-allowed, where $n = k$ or $n \neq k$. Due to the spherical symmetry of QDs, the oscillator strengths are independent of the electronic polarization direction and determined by the overlap integrals of the radial wavefunctions.

3. Results and discussion

The numerical parameters used in the calculations are: $\gamma_1 = 3.06, \gamma_2 = 0.85, \gamma_3$=1.25;[23] $m_{\rm e}$= 0.20;[24] $E_{\rm g}$=3.231eV;[25] ϵ=9.4;[26] $\Delta_{\rm so}$=0.017eV.[25] For several of the existing Luttinger values, we choose the moderate one from the long list in Ref.[27].

In order to reflect the relation between confinement energy and QD radius, the dependence of confinement on $(1/a^2)$ is always given. Figure 1 displays the calculated energies of valence-band, as well as the conduction-band state in spherical GaN QDs versus $(1/a^2)$. From Fig.1, we can see that the confinement energy of valence band is much smaller than that of conduction state, because the effective mass of holes are rather bigger than that of electrons. For the hole levels, when dots are in the strong confinement regime, i.e. the crystal radii are a few times smaller than exciton Bohr radii[15] (the effective exciton Bohr radius of GaN is about 3nm), confinement energies are changed nearly linearly with $1/a^2$, which gives a suitable relation as are needed in the calculations of the absorption spectra. When particles sizes are out of the confinement regime, the hole levels are tangled each other.

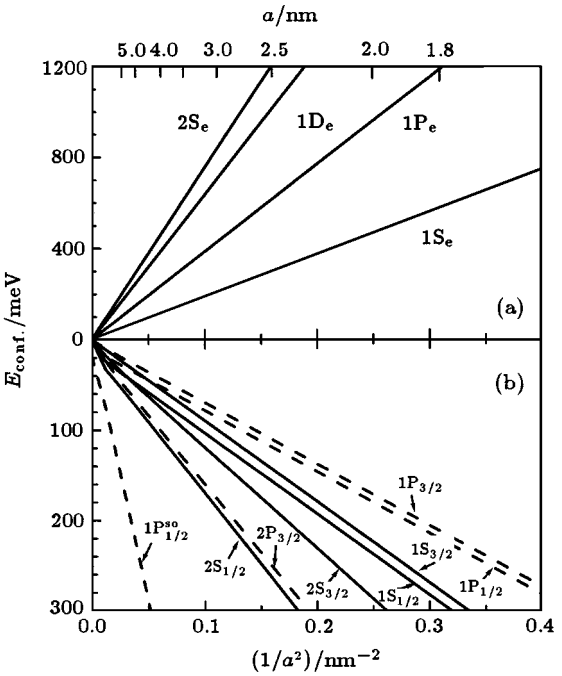


Fig.1. Plot of the calculated confinement energies of some conduction-band (a) and valence-band (b) levels in spherical GaN quantum dots versus $(1/a^2)$, where a is the dot radius. In valence-band levels, solid lines (dashed lines) represent levels for which interband transitions are allowed (forbidden) towards the $1{\rm S}_{\rm e}$ ground conduction-band level.

Table 1 gives the oscillator strengths for the dipole-allowed transitions for various sizes. Results show that, the oscillator strengths are only weakly size-dependent. When the variation of particle sizes is small, oscillator strengths can be treated as constants.

We can build the absorption spectrum in small nanocrystals, since we know the selection rules and the energy of optical transitions between the quantized energy levels of holes and electrons. Taking account of the Coulomb electron–hole interaction energy, we can write the energy of the transitions as[28]

$$\hbar\omega = E_{\rm g} + E_{\rm c} + E_{\rm v} - 1.786\, e^2/(\epsilon a) - 0.248 E^{*}_{\rm Ryd}, \quad (8)$$

where $E_{\rm g}$ is the band gap of bulk materials, $E_{\rm c}$ and $E_{\rm v}$ are the confinement energies of the conduction-band and valence-band states respectively. The fourth term is the Coulomb electron–hole interaction energy. $E^{*}_{\rm Ryd} = e^4/(2\epsilon^2\hbar^2(m_{\rm e}^{-1} + m_{\rm h}^{-1}))$ is the effective Rydberg energy.

Table 1. The oscillator strengths in units of $2P^2/m_0 = 2|\langle S|P_z|Z\rangle|^2/m_0$ for the dipole-allowed transitions in zinc-blende GaN quantum dots for various sizes. Only the transitions with a significant oscillator strengths are listed.

Transitions	Oscillator strength for different radius/nm				
	1.5	2.0	2.5	3.0	3.5
$1S_{3/2}$–$1S_e$	0.163	0.185	0.197	0.203	0.207
$3S_{3/2}$–$1S_e$	0.062	0.070	0.074	0.075	0.074
$1S_{3/2}$–$2S_e$	0.024	0.030	0.035	0.038	0.039
$1S_{1/2}$–$1S_e$	0.162	0.179	0.187	0.190	0.189
$2S_{1/2}$–$1S_e$	0.065	0.077	0.085	0.092	0.099
$1P_{3/2}$–$1P_e$	0.198	0.237	0.260	0.275	0.284
$2P_{3/2}$–$1P_e$	0.076	0.092	0.102	0.107	0.109
$1P_{1/2}$–$1P_e$	0.197	0.236	0.259	0.274	0.283
$1S_{3/2}$–$1D_e$	0.022	0.028	0.033	0.036	0.039
$1S_{1/2}$–$1D_e$	0.023	0.030	0.036	0.040	0.044

The absorption spectrum of GaN QDs may be calculated as follows. The optical-absorption coefficient of a single quantum dot is given by

$$\alpha(\hbar\omega) \sim \sum_i \frac{f_i \Gamma_i}{(\hbar\omega - \hbar\overline{\omega})^2 + \Gamma_i^2}, \qquad (9)$$

where f is the oscillator strength, $\overline{\omega}$ the transition frequency, and Γ_i the homogeneous half-width of the ith interband transition. The sum is taken over all the transitions from the filled levels to the unfilled ones. To compare the theoretical results with experimental measurements of real QD systems, however, one has to take into account the fact that there is always a certain distribution of dot sizes $f(r)$ around a mean value $\overline{a}$. Since the single-particle energies depend strongly on radius a, the size-distribution introduces a pronounced inhomogeneous broadening of the observed spectra. In QDs, which have discrete energy levels, the optical absorption coefficient $\alpha(\hbar\omega)$ is proportional to the oscillator strengths and the number of oscillators. Assuming there is a Gaussian distribution, the number of oscillators is determined by $g(r) = r^3 \,/\, \overline{a}^3 \times \exp[-(\, r - \overline{a}\,)^2/2\sigma^2] \,/(\sigma\sqrt{2\pi})$. Taking account of the relation between the transition energy and the radius of dots, a relation $g(r(E))$ is obtained. Then the optical absorption coefficient is given by $\alpha(\hbar\omega) \sim \sum_i f_i\ g(E)$. When the size deviation is considerable, the homogeneous broadening can be neglected, and the continuous spectrum resulting from size-distribution may be considered as that of real QD systems.

Figure 2 shows a calculated linear absorption for zinc-blende GaN QDs compared with the experimental absorption spectrum in Ref.[5]. Theoretically, we adopt the homogeneous half-width of 10meV, a Gaussian distribution around $\overline{a}$=2nm with an absolute deviation 0.6nm at a confidence level 99%. Note that the average radius 2nm accords with the data in Ref.[5] which only presented a rough average radius. Because the size distribution of QDs in Ref.[5] is unknown, it is difficult to have the agreement of very good quality. Nevertheless, the theoretical absorption edge agrees well with the experimental result.

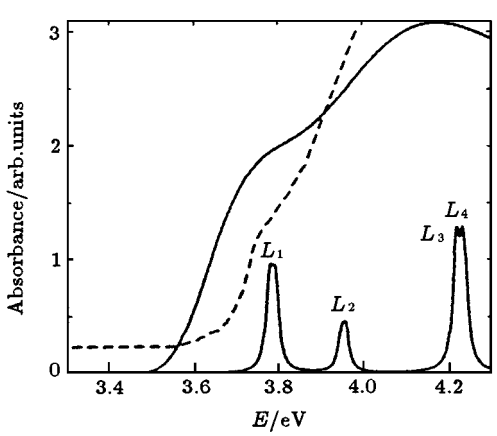


Fig.2. Calculated (solid line) and experimental (dashed line adopted from Ref.[5]) absorption spectra of zinc-blende GaN QDs. The top solid line is for a collection of QDs with a Gaussian size-distribution at an average radius 2nm, absolute deviation 0.6nm and confidence level 99%; the bottom solid line is for single QD with a homogeneous half-width of 10meV. L_1 corresponds to transitions $1S_{3/2} \longrightarrow 1S_e$ and $1S_{1/2} \longrightarrow 1S_e$, which can be distinguished by higher resolution. L_2 corresponds to transitions $3S_{3/2} \longrightarrow 1S_e$ and $2S_{1/2} \longrightarrow 1S_e$. L_3 and L_4 correspond to $1P_{3/2} \longrightarrow 1P_e$, $1P_{1/2} \longrightarrow 1P_e$ respectively.

4. Conclusion

In this paper, we studied the electronic structure of spherical zinc-blende GaN QDs using the multiple-band effective mass approximation and taking account of the strong spin–orbit coupling. The symmetry classification and energies of the electron and hole levels are obtained. When the radius of the quantum dots decreases, there appears a series of quantum size effects. The selection rules and oscillator strengths for optical transitions between the quantized hole and electron energy levels are given. Absorption spectra are obtained theoretically which are in good agreement with the existing experimental spectra.

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