Volume 8, Number 11
1004-423X/1999/08(11)/0845-08

ACTA PHYSICA SINICA
(Overseas Edition)

November, 1999
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SIZE AND SHAPE DEPENDENCE OF THE LOWEST CONDUCTION BAND STATES IN GaAs QUANTUM DOTS*

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(Received 27 April 1999; revised manuscript received 21 1999)

Using a recently developed new scheme, we investigated the electronic structure of the lowest conduction band states of cuboid GaAs quantum dots with different shapes and sizes in a wide range from 4 to 120a (a is the lattice constant). The critical edge length of the direct/indirect crossover in GaAs cuboid quantum dots depends on the size and shape of the quantum dots. As a deduction we also discussed the critical size of direct/indirect transition in GaAs quantum wires and thin films.

PACC: 7320; 7340L

I. INTRODUCTION

As one of the most fundamental problems in low dimensional physics, quantum confinement effects have been investigated intensively in recent years,[1] with the progress in the fabrication of semiconductor nano-structures. Various theoretical methods have been developed to treat those effects. The effective mass approximation (EMA) approaches have been playing a very important role in our understanding of the quantum confinement effects, but numerically they always overestimate the gap of quantum dots[2] and their applications are limited to large quantum dots. On the other hand, the direct calculation approaches based on pseudopotential methods or linear combination of atomic orbitals methods,[3] usually provide numerical results in much improved agreement with experimental data over the EMA, but those approaches can hardly treat the dot sizes of interest in many practical problems. Recently we developed a simple new approach,[4] in which the expectation energy levels in low dimensional systems are obtained by doing integrations in the Brillouin zone

*Project supported by the State Key Laboratory of GaAs Integrated Circuits of China, the National Natural Science Foundation of China (Grant Nos. 19574008 and 19774001), the National "Climb" Program on the Science and Technology of Nanomaterials, China.
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rather than solving the Schrödinger differential equation in real space. Numerical calculations for an exactly solvable example indicate that this simple scheme greatly improve upon the EMA based methods very much in the numberical accuracy[4] and upon the direct solving methods in the treatable dot size by significantly reducing the computing efforts. We have used this new developed approach to investigate the quantum size effect of GaAs cubic quantum dots. In this work we extended our previous work and investigated, over a wide range, the electronic structure of the lowest conduction band states of cuboid GaAs quantum dots with square cros section, focusing on the size and shape dependence of the electronic structure.

Many previous theoretical calculations mainly investigated quantum dots with highly symmetrical shape. Less theoretical paper treated quantum dots of irregular shape.[5,6] In this work we investigate cuboid GaAs quantum dots with their surfaces perpendicular to the x, y, z axes in [100], [010] and [001] directions. The lengths of the three sides of the cuboid are L_x, L_y and L_z, where $L_x = L_y \neq L_z$. Different from spherical or cubic quantum dots, the degeneracy in X (or Y) and Z directions is lifted in cuboid dots because of the lower symmetry. Thus the energies of X_{1c} valley in k_x-axis and k_z-axis are no longer identical. We calculated the size and shape dependence of the Γ_{1c}-like energy and the X_{1c}-like energy minima of lowest conduction band states in k_x-axis and k_z-axis, which originate from the satellite valleys in bulk Δ axis, locating at $(\pm k_c, 0, 0)$ or $(0, 0, \pm k_c)$, where $k_c \approx 0.91 \cdot \frac{2\pi}{a}$ (a is the lattice parameter). Hereafter we denote them as $X_{1c,x}$, $X_{1c,z}$, respectively.

II. THEORETICAL METHOD

The approach we recently developed[4] is essentially a scheme of trying to obtain the expectation values of confined Bloch states from the knowledge of the corresponding bulk Bloch waves–in the simple case we discussed here, from the corresponding dispersion relation of the bulk. The EMA basically is also an approach using the bulk information, but it uses only the curvature of $\varepsilon(\boldsymbol{k})$ dispersion relation of the bulk. Our scheme uses much more and thus can give much improved numerical results than the EMA based methods.

The discrete energy levels in quantum dots can be expressed by the bulk dispersion relation and the confined states in terms of Bloch states of the bulk material as[4]

$$E_{\alpha,j} = \sum_n \int_{\text{B.Z}} |\langle n, \boldsymbol{k}|\alpha, j\rangle|^2 \varepsilon_n(\boldsymbol{k}) \mathrm{d}\boldsymbol{k}, \tag{1}$$

here $\int_{\text{B.Z}}$ means that the integral is over the Brillouin zone, α classifies the electronic states (Γ_{1c}-like, $X_{1c,x}$-like or $X_{1c,z}$-like etc.), and j labels the ordering of the states in the α classification, n labels different branches of the bulk energy spectra, while $\varepsilon_n(\boldsymbol{k})$ is corresponding to bulk electronic structure. In this work we are only interested in the lowest Γ_{1c}-like, $X_{1c,x}$-like or $X_{1c,z}$-like confined states. Thus we always choose $j = 1$.

In this paper, we used two approximations to Eq. (1):

1. We neglect the branch mixing effect. Branch mixing modifies the wave function in small size crystals. But for the smallest size discussed in this work, $L = 4a \approx 2.3\,\text{nm}$, based

our experience on the quantum confinement of lowest conduction states in Si dots[7], this effect will not exceed a few percent. Therefore, we use only the lowest conduction band structure $\varepsilon_c(\boldsymbol{k})$ of bulk GaAs in calculating the quantum confinement effect of different valleys in the lowest conduction band, thus turn Eq. (1) to

$$E_{\alpha,1} = \int_{\mathrm{B.Z}} |\langle c, \boldsymbol{k}|\alpha, 1\rangle|^2 \varepsilon_c(\boldsymbol{k}) \mathrm{d}\boldsymbol{k} . \tag{2}$$

2. We simplify the expansion coefficients $\langle c, \boldsymbol{k}|\alpha, 1\rangle$ as products of analytical functions $c_{j_i}(k_i)$, with proportionality constant A_α,

$$\langle c, \boldsymbol{k}|\alpha, 1\rangle = A_\alpha c_{j_1}(k_1) c_{j_2}(k_2) c_{j_3}(k_3) , \tag{3}$$

here $c_{j_i}(k_i)$ is defined as

$$c_{j_i}(k_i) = \frac{j_i \sqrt{\pi L_i}}{j_i^2 \pi^2 - k_i^2 L_i^2} \left(\exp\left(-ik_i \frac{L_i}{2} \right) - (-1)^{j_i} \exp\left(ik_i \frac{L_i}{2} \right) \right) , \tag{4}$$

L_i is the edge length of the quantum dot in i direction.

As explained in Ref.[4], $c_j(k)$ is the expansion coefficients of the standing wave of $j-1$ nodes in the representation of plane waves. $|c_1(k)|^2$ peaks at $k=0$, but other $|c_j(k)|^2$ peaks near $k = \pm j\pi/L$ as j increases. A_α can be determined by the normalization.

The integer j_i in Eq. (3) depends on α. For the $\Gamma_{1,c}$ state we have $j_1 = j_2 = j_3 = 1$. For the $X_{1c,x}$ state we have $j_1 = j_x$, $j_2 = j_3 = 1$ and for the $X_{1c,z}$ state we have $j_1 = j_2 = 1$, $j_3 = j_z$. The integers j_x and j_z can be appropriately chosen, depending on L_x/a and L_z/a: We take several values of j_x around $0.91 \cdot 2L_x/a$, for which $|c_{j_x}(k_x)|^2$ peaks near the $X_{1c,x}$ valley originating from the satellite valley in bulk Δ_x axis, to do the calculation and choose the one that gives the X_{1c}-like energy minimum of the lowest confined state in k_x-axis. j_z can be chosen in similar way.

We use the lowest conduction band structure of bulk GaAs obtained by empirical pseudopotential method (EPM)[8] as $\varepsilon_c(\boldsymbol{k})$ in Eq. (2). Thus, the energy levels of Γ_{1c}-like, $X_{1c,x}$-like and $X_{1c,z}$-like states in GaAs quantum dots can be obtained simply by doing integrals in the Brillouin zone.

III. QUANTUM CONFINEMENT EFFECT

We are mainly interested in the shape and size dependences of Γ_{1c}-like, $X_{1c,x}$-like and $X_{1c,z}$-like states in GaAs quantum dots.

Fig.1 (a)–(d) show the L_z dependences of energies of Γ_{1c}-like, $X_{1c,x}$-like and $X_{1c,z}$-like conduction band states when $L_x = L_y = 120, 20, 6, 5a$, respectively. Fig.2(a)–(d) show the $L_x(L_y)$ dependences of energies of Γ_{1c}-like and X_{1c}-like conduction band states when $L_z = 120, 20, 5, 4a$, respectively. In both Fig.1 and Fig.2, the largest edge length of the GaAs quantum dots is $120a$, i.e., approximately 67.8 nm

Different from cubic quantum dots treated before,[4] in cuboid quantum dots where $L_x = L_y \neq L_z$, the decrease in symmetry leads to the lift of the degeneracy of X_{1c}-like states in [100] and [001] directions, making their size dependences split into two lines, which are denoted as $X_{1c,x}$ and $X_{1c,z}$ in Figs.1 and 2. These two lines intersect at $L_x = L_z$.

As we noticed, in Fig.1, when $L_z < L_x$, the energy of $X_{1c,x}$ is higher than that of $X_{1c,z}$. By looking at the shape of the ellipsoid valley of GaAs in [100] direction and [001] direction, we can see this is a natural consequence of the anisotropy of ellipsoids in X_c valleys.

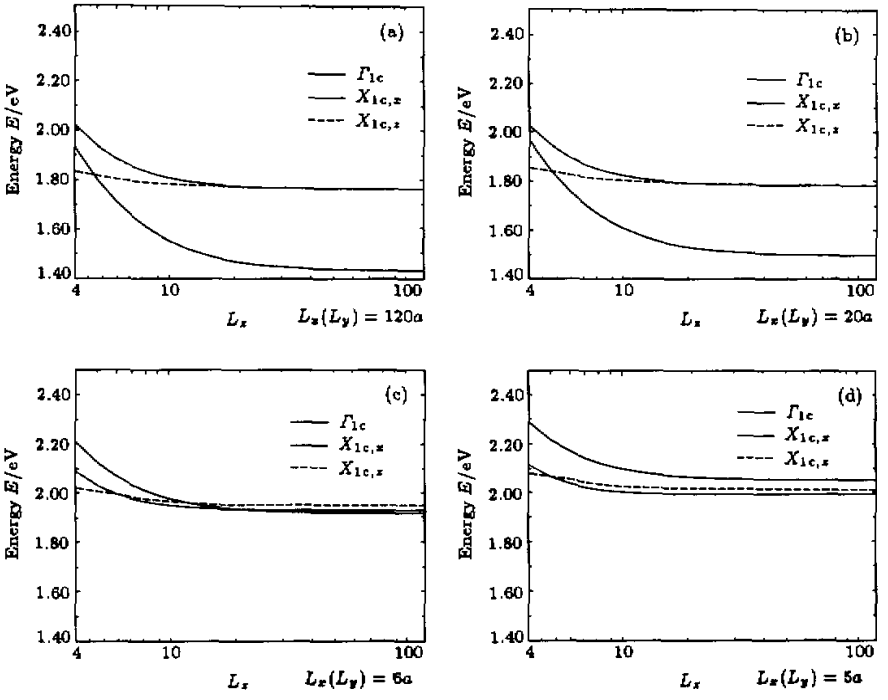

Fig.1. The energies of Γ_{1c}-like and X_{1c}-like conduction band states as the functions of L_z, when $L_x(L_y)$ is fixed at (a) $120a$, (b) $20a$, (c) $6a$ and (d) $5a$, respectively.

We can give a qualitative explanation of the result of Fig.1 and Fig.2 based on the anisotropy of the constant-energy surface of each valley. Fig.3 shows the distribution of $|\langle c, k_z|X_{1c,z}, 1\rangle|^2$ which corresponds to the lowest GaAs $X_{1c,z}$-like state. It concentrates near $(0, 0, 0.91)\cdot\frac{2\pi}{a}$, so in calculating the integral of the $X_{1c,z}$-like state in Eq. (2), the band structure near $(0, 0, 0.91)\cdot\frac{2\pi}{a}$, the ellipsoid valley in k_z axis of GaAs plays a dominating role. On the other hand, in calculating the integral of the $X_{1c,x}$-like state in Eq. (2), the band structure near the ellipsoid valley in k_x axis of GaAs plays a dominating role. Fig.4 shows ellipsoid valley A on k_x-axis and ellipsoid valley B on k_z-axis. When confined in L_z direction, the two ellipsoid valleys exhibit quite different quantum confinement effects: The effective mass of valley A in z direction is less than that of valley B, so the quantum confinement effect is stronger. Thus in Fig.1, with the decrease of L_z, the energy of $X_{1c,x}$ increases faster than that of $X_{1c,z}$, demonstrating stronger quantum confinement effect: When $L_x = L_y$ is fixed, the rise of $X_{1c,z}$ valley mainly depends on the effective mass in z direction of B valley,

which is larger. However the rise of $X_{1c,x}$ valley mainly depends on the effective mass in z direction of A valley, which is smaller. In case of Fig.1, where $L_x = L_y$ is fixed, variation comes from the change of L_z, as a result, the A valley on k_x-axis shows a stronger effect.

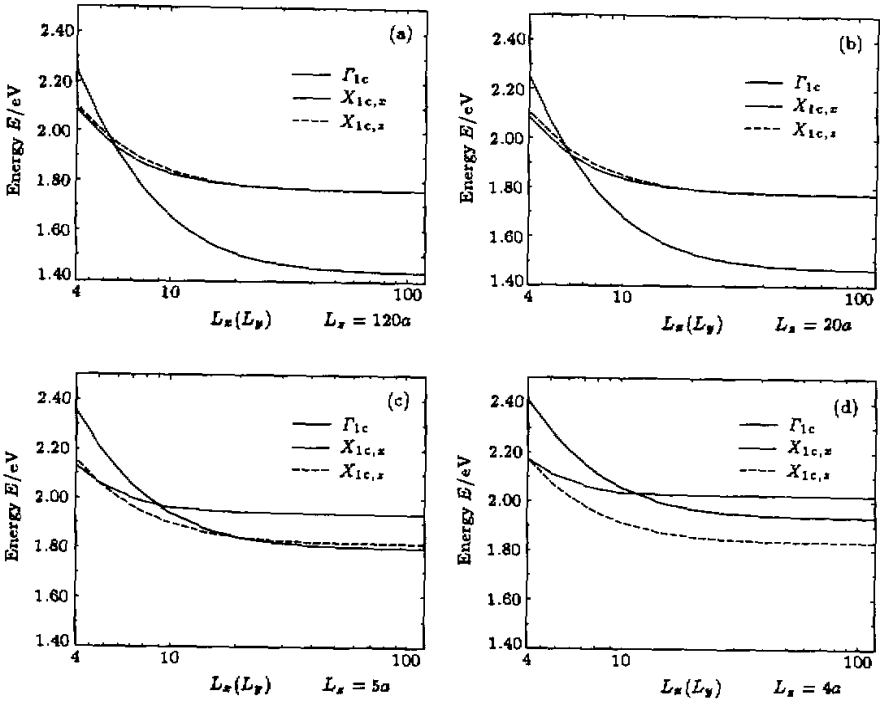

Fig.2. The energies of Γ_{1c}-like and X_{1c}-like conduction band states as the functions of $L_x(L_y)$, when L_z is fixed at (a) $120a$, (b) $20a$, (c) $5a$ and (d) $4a$, respectively.

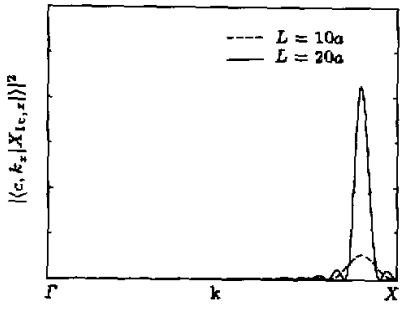

Fig.3. The main peak of $|\langle c, k_x|X_{1c,x}, 1\rangle|^2$ corresponding to GaAs X_{1c}-like state.

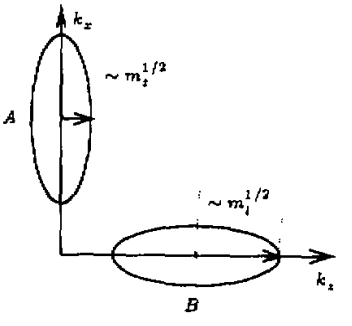

Fig.4. Different extent of quantum confinement effect exhibited by two valleys, when confined in L_z direction.

Based on the same reason, in Fig.2, when $L_x < L_z$, the $X_{1c,z}$ energy is higher than $X_{1c,x}$ energy.

Bulk GaAs is a well known direct semiconductor, in which both the conduction minimum and the valence band maximum locat at the Γ point of the Brillouin zone. In GaAs quantum dots, because the quantum confinement effects of Γ_{1c}-like valley and X_{1c} valley are quite different, as shown in Fig.1 and Fig.2, so that the Γ_{1c}-like conduction band state may be not the lowest conduction band state. If this happens, then the GaAs quantum dot becomes an indirect semiconductor. In Figs.1 and 2, the intersection of the Γ_{1c} line and the lower one of $X_{1c,x}$ and $X_{1c,z}$ line is the critical point of the direct/indirect transition of GaAs quantum dots. The transition points of L_z corresponding to various $L_x(L_y)$ are listed in Table 1. When $L_x(L_y) = 5a$, the Γ_{1c} line is always higher than the $X_{1c,x}$ line and $X_{1c,z}$ line, indicating that the GaAs quantum dots are always indirect rather than direct as in the bulk. Thus, in cuboid quantum wires with surface planes oriented in the [100] and [010] directions, direct/indirect crossover happens when $5a < L_x(L_y) < 6a$.

Table 1. The critical points of L_z corresponding to various $L_x(L_y)$(unit:a).

$L_x(L_y)$	120	100	40	20	10	8	6	5
L_z	4.84	4.84	4.87	4.99	5.72	6.49	20.11	∞

Table 2. The critical points of $L_x(L_y)$ corresponding to various L_z(unit:a).

L_z	120	100	40	20	10	8	6	5	4
$L_x(L_y)$	5.83	5.83	5.87	6.00	6.56	6.94	8.90	19.43	∞

When $L_x(L_y)$ in Fig.1 is large enough, for instance, $L_x(L_y) = 120a$, the result of calculation can also be approximately regarded as the result of GaAs thin film with its surface planes perpendicular to the [001] direction. According to Table 1, the direct/indirect change takes place when the thickness of the GaAs thin film grown in [001] direction is $4.84a$, or 2.7 nm.

Results of direct/indirect crossover of various L_z are listed in Table 2. As the same as in the Fig.1 and Table 1, when L_z is large enough, for example, $L_z = 120a$, the directindirect transition thickness can be considered as the direct-indirect transition thickness of GaAs quantum wire as well. From Table 2, we can see that this happens when $L_x(L_y) = 5.83a$, or 3.3 nm. This confirms what we just said: in GaAs cuboid quantum wires with surface planes oriented in the [100] and [010] directions, direct/indirect crossover happens when $L_x(L_y)$ is between $5a$ and $6a$.

The major error in our calculations is due to the fact that the integral in Eq. (2) is only in the Brillouin zone, while $c_{j_i}(k_i)$ in Eq. (4) is expanded in the whole k space. By inspecting Fig.3, we see the main peaks of $c_{j_x}(k_x)$ in Eq. (4) is in the first Brillouin zone, so we can expect that the error introduced by the substitution would not be large. Numerical calculations indicate that[4], using this approximation, the error is much smaller than that of EMA method.

Franceschetti and Zunger[5] calculated critical sizes for the direct-indirect transition in free standing GaAs films, wires and dots. But the surface orientation of the films, wires and dots they calculated are different from one we calculated here. It might be interesting to compare their results with ours.

The surface orientation of free standing GaAs films Franceschetti and Zunger calculated is $[1,-1,0]$ and the critical size they obtained is 1.6 nm A critical size of 2.7 nm is obtained for film surface oriented in [0,0,1] direction. The effect of surface orientation difference in our case can be clearly qualitatively understood from our Fig.1(a). The critical size will basically be determined by the Γ-L dependence and the lowest X_{1c}-L dependence (L is the film thickness). These is basically no orientation effect of the Γ-L dependence for thin films, because the Γ valley of bulk GaAs is isotropic. Thus the orientation effect of the critical size is only determined by the lowest X_{1c}-L dependence. However the lowest X_{1c}-L dependence for $[1,-1,0]$ oriented films should be between the dashed line (approximately determined by m_l) and the dotted line (approximately determined by m_t). Thus the quantum confinement effects of the $X_{1c,x}$ and $X_{1c,y}$ valleys should be stronger than the one approximately determined by m_l only but weaker than the one approximately determined by m_t only. However the quantum confinement effects of $X_{1c,z}$ valleys should be approximately determined by m_t as shown as the dotted line in Fig.1(a). Thus the critical size of $[1,-1,0]$ oriented GaAs films should be smaller than the one of [0,0,1] oriented films. Similarly from Fig.2(a) it is understandable that the critical size of the [1,1,0] and $[1,-1,0]$ oriented GaAs wires (obtained by Franceschetti and Zunger as 2.8 nm) should be smaller than the one of the [1,0,0] and [0,1,0] oriented wires (our result is 3.3 nm).

IV. CONCLUSIONS

In summary, by using a newly developed simple scheme, we have investigated the size and shape dependences of Γ_{1c}-like and X_{1c}-like confined states in GaAs free standing cuboid quantum dots. We obtained the direct-indirect transition critical sizes for free standing GaAs films oriented in [0,0,1] direction and for free standing GaAs wires with surfaces oriented in [1,0,0] and [0,1,0] directions. Those critical sizes are qualitatively in agreement with the critical sizes obtained by Franceschetti and Zunger for GaAs quantum wires and films with different orientations.

ACKNOWLEDGMENTS

S. Y. Ren is grateful to Professor Kun Huang and Professor John D. Dow for stimulating discussions. The authors thank Prof. Jian-bai Xia for sending us an EPM computing code to calculate the bulk GaAs band structure.

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