Effect of strain and quantum confinement on the electronic and optical properties in CdTe/ZnTe core/shell QDs

ZHANG WEI, FEI XUENING, WEI XIAOYIN, DONG ERMING, TANG HAO, JIA GUOZHI*
Tianjin Chengjian University, Tianjin China

The electronic structures of CdTe/ZnTe core/shell structure quantum dots (QDs) has been investigated using the single-band effective mass approximationand first-order perturbation approximation theory. The electronic structure of CdTe/ZnTe QDs is a typical type-II band structure, andthe electron and hole carries would be localized in the core and shell regions respectively. The overlap integral of wave function of them and bandgap energy vary with the changing of core radius and/or shell thickness due to quantum confinement effect. The electronic and optical properties could be tuned by varying the size of QDs.

(Received February 12, 2015; accepted March 19, 2015)

Keywords: Core/shell, Quantum dots, Strain effect, CdTe/ZnTe

1. Introduction

Recently, semiconductor nanoparticles have attracted a large of attentions due to their uniqueoptical and photoelectrical properties. These novel properties are mainly caused by the high surface-to-volume ratio or the three-dimensional confinement of carriers in the low dimensional structure [1]. Due to these new proprieties, semiconductor nanoparticles have many potential applications in light-emitting devices [2], biological tagging materials [3], quantum dot lasers [4], and solar cells [5].

As for the core/shell nanostructures, QDs are classified as type-I or type-II structures depending on the band-edge relativealignment of valence/conduction band at the heterointerface. In type-I structure, both the electron and hole localized in the same region due tothe edges of conduction and valence band of this semiconductorare located within the energy gap of the other one (shell) [6]. In the type-II case, carriers are spatially separated into different ranges of the core/shell QDs because the lowest energy states for electrons and holes are in different layers.The "spatially indirect" energy gap of type-II structure QDs is determined by the edgesof conduction- and valence-band of the two different semiconductors, which is smaller than either the core or shell materials. Thus, type-II structure QDs can emit longer wavelength [2] and slow the Auger and radiative decay lifetime. The controllable spatial separation of holes and electrons provides new ways to make the QDs available for photovoltaic or photoconduction applications.

Many works about the semiconductor nanoparticles have been done by experimental or theoretical methods as strain-tunable colloidal nanocrystals had been synthetized by epitaxial deposition [7], the self-assembling method [8], the pressure studied by using a variational method [9] and theoretical models using effective mass approximation and first-order perturbation theory [6]. Itis found that the lattice-mismatch at the hetero interface, the changes of thickness of particles, the effective masses and the dielectric constants can influence the properties of nanoparticles obviously. A large numbers of studies have investigated the effect of strain induced by lattice-mismatch of core and shell to the QDs [8], which can be substantially changedboth the conduction and valence band energies, the possibilities of location of carriers and electronic and optical properties [7].

Here, we present the effect of strain ona type-II structure QDs CdTe/ZnTeby varying the ratio of core radius and shell thickness. The electron structure, band alignment, and overlap integral with taking into the coulomb interaction account are studied by using the simple effective mass approximation modeland first-order perturbation approximation. The wave function behaviors of electron and hole in core/shell QDs are investigated by changing the radius of core and/or thickness of shell. The bandgap energy, the wave function of electrons and holes and the overlap of them is analyzed in detail.

2. Theory

Here, we assume that the core/shell QDs is a concentric sphere, that is to say, CdTe core is epitaxially capped with a concentric ZnTe shell and all interfaces are assumed to be mutational heterojunction [10]. The energy

band lineups of CdTe/ZnTeQDs are first analyzed by model-solid theory with taking the effects of strain into account.Strain plays a key role in changing the energy levels of core/shell structure QDs which is always caused by the different lattice parameters of core and shell. The lattice constant of ZnTe (a=6.08Å) has a little difference to CdTe (a=6.48Å), the CdTe core could be capped with a ZnTe shell coherently, the lattice parameters and strain of core/shell at the heterointerface are calculated as follows [11],

$$a_{\square} = \frac{a_1 G_1 R + a_2 G_2 H}{G_1 R + G_2 H} \tag{1}$$

$$a_{\perp} = a_2[1 - D(a_{\square} / a_2 - 1)] \tag{2}$$

$$\in_{\perp/\square} = a_{i\perp/\square} / a_i - 1 \tag{3}$$

where R is the radius of CdTe, H is the thickness of ZnTe, the lattice constant is denoted by a, $\in$ is the strain tensor, G is the shear modulus and D is a constant depending on the elastic constants c_{11}, c_{12} and c_{44} which are given in elsewhere [13]. The subscripts $\perp$ and $\square$ denote the quantities parallel or perpendicular to the interface plane, i indicates the semiconductor 1 (stands for core) or 2 (shell).For the spherical symmetry CdTe/ZnTe QDs, the core was "squeezed" and the shell "stretched" because of the different lattice parameters. In the core region, the compressive stressinduced by shell is the same in parallel and perpendicular directions to the interface plane, so the lattice parameters and strain is the same in these two directions and calculated by equation (1) and (3) respectively. At the ZnTe shell, the strain in parallel direction to the interface is calculated by equation (1) and in perpendicular direction by equation (2).

In the core/shell QDs, the Schrodinger equation of carriers is given as:

$$\left(-\frac{\hbar^2}{2}\nabla\frac{1}{m_i}\nabla - V(r)\right)\Psi(r) = E\Psi(r) \tag{4}$$

where $\hbar$ is Planck's constant divided by 2π, m_i is the particle mass and $V(r)$ is potential that are both depending on the position in the QDs, E stands the energy eigenvalue and $\psi(r)$ the corresponding eigen function. Using the single-band effective mass approximation, the Schrodinger equation issolved with taking the space-dependent effective mass of carriers into account.Weassume that the QDs is spherically symmetric and the potentials is homogeneous, so the wave functions of carriers can be separated into radial and angular parts as follows [12,13,14],

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi) \tag{5}$$

and the solutions must satisfied the boundaries,

$$R_{nl,i}(_i r_i) = R_{nl,i+1}(r_i) \tag{6}$$

$$\frac{1}{m_i}\frac{dR_{nl,i}(r_i)}{dr}\bigg|_{r=r_i} = \frac{1}{m_{i+1}}\frac{dR_{nl,i+1}(r_i)}{dr}\bigg|_{r=r_i} \tag{7}$$

where $R_{nl,i/i+1}(r)$ is the radial wave function of carriers and $Y_{lm}(\theta,\phi)$ a spherical harmonic.

On the basis of first-order perturbation approximation, the coulomb interaction energy can be regarded as a heliumlike perturbationand written as equation (8) after expanding of $1/(|r_e - r_h|)$ in spherical harmonics form and integrating over the angular coordinates [13].

$$E_c = -\frac{e^2}{4\pi\varepsilon_0}\iint dr_e dr_h r_e^2 r_h^2 \frac{|R_e(r_e)|^2 |R_h(r_h)|^2}{\max(r_e, r_h)\bar{\varepsilon}(r_e, r_h)} \tag{8}$$

where $\bar{\varepsilon}$ is the mean dielectric constant.

After solving the wavefunction of electron and hole carriers, the overlap integral which relating the ability of the holes and electrons to directly recombine is defined as

$$\Theta = \left|\int_0^{R+H} r^2 \psi_{lm}{}^{\theta}(r)\psi_{lm}{}^{h}(r)dr\right|^2 \tag{9}$$

where $\psi_{lm}^{\theta(h)}(r)$ is the radial part of the electron (hole) envelope wavefunction which has been normalized to unity.

3. Result and discuss

The band alignment of CdTe/ZnTe core/shell QDs with different shell layer thickness are illustrated in Fig. 1. In the bulk materials, the relative valence band energy of

CdTe is higher than ZnTe 0.1eV [11] and the natural band alignment of them are showed as the left structure in Fig. 1 which belongs to the type- I structure and localize both electrons and holes in CdTe core. When a compressible nanocrystalline CdTe core was capped with a ZnTe shell coherently, the bandgap energy would be changed significantly by lattice strain. No matter a thin or thick core covered with a certain shell, the band alignment would change to type-II structure. The holes are localized in the shell while the electrons in the core in theoretically, and the energy gap is "spatially indirect". The differences of these two statesarerelative band energy and bandgap energy, which responding to the possibilities of presence of carriers in the QDs and the electronic and optical properties.

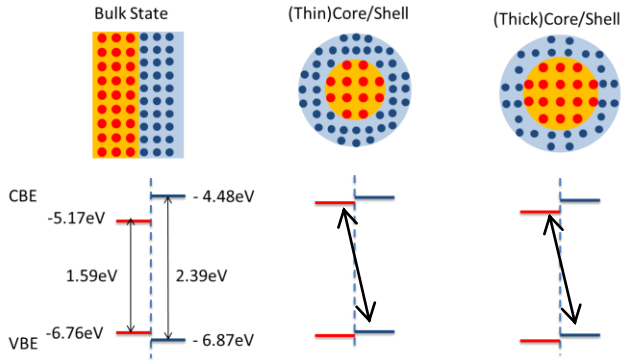

Fig. 1. Schematic diagram of band alignment of CdTe/ZnTe core/shell QDs in different structures induced by lattice strain. The upper islattice structures from left to right: ordinary bulk CdTe-ZnTe material, a thin core CdTe/ZnSe QDs (squeezed core with strained shell) and a thick core QDs (strained core with stretched shell). The followingare electronic band energy levels of each state, respectively. The carries are spatially separated into the shell (holes)or core (electrons) in QDs state and it isa classical type-II structure.

Due to the lattice constant of ZnTe (6.08 Å) smaller than CdTe(6.48 Å), the core has been "squeezed" by the compressive force, and the shell has been "stretched" with the impact of tensile stress. These two strain effects work together to alter the energy band offsets and result in a spatial separation of carriers. The strain and band offsets change with the increasing of core radiuswhich has been shown in Fig. 2. The calculation method uses the model-solid theory and a continuum elasticity model without taking the quantum confinement into account. Here, we assume that the strain of shell is a constant value and no change with the radius from center to boundary [10]. From Fig. 2, it can be seen clearly that the strain of core decreases with the increasing of core radius, whilethe one in the shell increasesin both the perpendicular and parallel directions to the interface plane. The energy gap would increase under compressive strain and decrease with tensile stress for II-VI semiconductors with zinc-blende structures, which has been observed by experiment and been theoretically predicted [15]. The conduction band energy of core descends due to decreased compressive strainand the shell's decreases because of the increasing tensile stress as the increasing of shell thickness, which is shown on the right part of Fig. 2, and the shift of conduction band is larger than the valence band [16]. As a result of them, the electronic and optical properties would be changed obviously, such as the absorption and emission band edges. All the parameters we used are listed in Table 1.

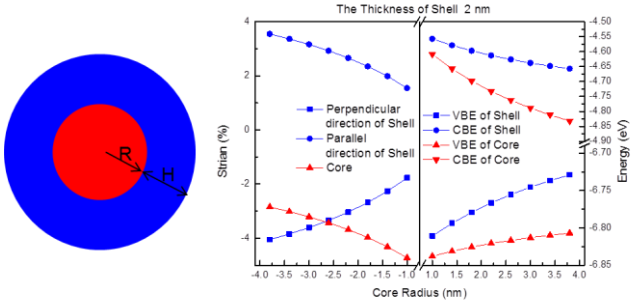

Fig. 2. The strain and band shifting of a changing CdTe core capped with a certain ZnTe shell of 2nm. On the left is the changing of strain and on the right is band energy shifting with the radius of core changing from 1 to 4 nm. As the core radius increasing, the conduction band energy (CBE) of both the core and shell descends, while the valence band energy (VBE) increases.

Tabel 1. The parameters ofCdTe and ZnTe material. Lattice constant a, deformation potentials b, and the values of parameters G and D for (001) orientation; A is given in Å*, G is given in Mbar; D is dimensionless, m_e is the effective mass of electrons, $m_h$is the effective mass of holes.*

Material	a	D	G	m_e/m_0	m_h/m_0	Dielectric constants	Band gap (eV)
ZnTeCdTe	6.08	1.142	1.311	0.11	0.7	7.78	2.39
	6.48	1.402	0.807	0.14	0.37	9.4	1.59

In the following, the probability density of electrons and holes in CdTe/ZnTe QDs has been shown in Fig. 3. It can be seen clearly that the electrons are localized in the core region while the holes are confined in the shell, which is a classical type-II structure QDs. In order to investigate the effect of strain on the distribution of carriers, we simulated a series of QDs with different core radius and fixed values of shell thickness (2nm) and the wavefunction of electrons and holes in them had been computed and shown in Fig. 4. From left to right, the radius of core varies as 2.8, 3.1, 3.4, 3.7, 4 nm, respectively. For small core radius, because of the small relative valence band energy between core and shell, the wavefunction of holes is concentratedto the heterointerface and the "peak" of wavefunction of electrons and holes are close to each other, which result in a high overlap value showed in Fig. 5. With the increasing of the core radius, the wavefunction of holes moves towards to the boundary and becomes sharper; it is mainly because of the competition between kinetic energy and potential energy [12]. Due to the band offsets and carrier effective masses, when the core radius becomes larger, the tensile stress of shell increase, the deformation potential would confine the holes stronger in the shell region,resulting in the carriers shift towards the boundary [12]. The electrons are localized in the core, while the peak of wavefunction flattening out. It can be clearly seen that, the strain and quantum confinement effect have important influence to tuning the distribution of carries in the region of QDs, and the overlap values descend from 0.9 to 0.1 with the increasing of core radius as shown in Fig. 5.

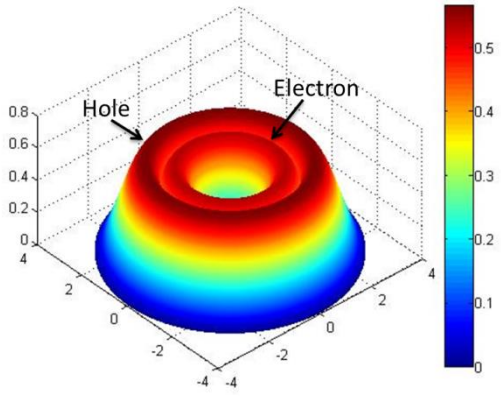

Fig. 3. Schematic diagram of the probability density of carriers in ZnSe/ZnTe QDs. The particle is keeping a size constant with both the core radius and shell thickness 2 nm.

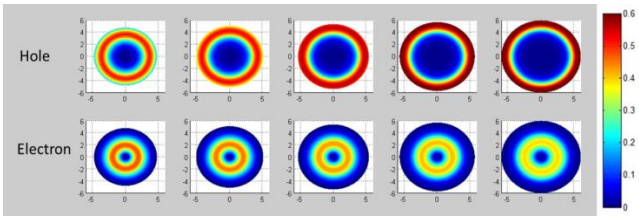

Fig. 4. The probability density of electrons and holes in CdTe/ZnTe QDs with a fixed value of shell thickness (2 nm) as a function of core radius, which is 2.8, 3.1, 3.4, 3.7, 4 nm, respectively.

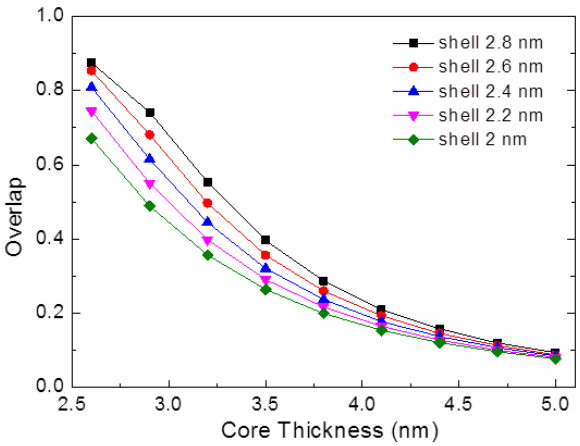

Fig. 5. The overlap integral of wave functions in CdTe/ZnTe QDsas a function of the core radiusvaried from 2.6 to 5 nm with the shell thickness of 2, 2.2, 2.4, 2.6, 2.8 nm, respectively. It could be seen clearly that the overlap integral descends from 0.9 to 0.1 with the increasing of core radius.

4. Conclusion

In conclusion, the electronic structures of CdTe/ZnTe core/shell structure QDs has been investigatedthroughthe theoreticalcalculation with taking the coulomb interaction into account. It is found that the electron and hole carries would localized in the core and shell regions as spatially separatedrespectively, and the overlap integral of wavefunction of them varies with the changing of core radius and/or shell thickness. The electronic structure of CdTe/ZnTe QDs is a typical type-II band structure and the "spatially indirect" gap energy changes from 1.89 to 2.22 eV, that is to say, the electronic and optical properties could be tuned by varying the size of QDs based on the quantum confinement effect.

Acknowledgements

This work has been partly supported by the National Natural Science Foundation of China (11147024, 11247025, 51208334), Tianjin Construction Committee Science Technology Project (2014-23), Tianjin Natural Science Foundation (14JCTPJC00480, 14JCNJC07800), and the General Project of Humanities and Social Science Research of Education Ministry (11YJCZH202).

References

[1] Brusle, The Journal of Chemical Physics **79**, 5566 (1983).
[2] J. Bang, J. Park, J. H. Lee, et al, Chemistry of Materials **22**, 233 (2009).
[3] W. C. Chan, S. Nie, Science **281**, 2016 (1998).
[4] V. Klimov, A. Mikhailovsky, S. Xu, et al, Science **290**, 314 (2000).
[5] R. Laghumavarapu, M. El-Emawy, N. Nuntawong, et al, Applied Physics Letters **91**, 243115 (2007).
[6] S. A. Ivanov, A. Piryatinski, J. Nanda, et al, Journal of the American Chemical Society **129**, 11708 (2007).
[7] A. M. Smith, A. M. Mohs, S. Nie, Nat Nanotechnol **4**, 56 (2009).
[8] K. Nishi, H. Saito, S. Sugou, et al, Applied Physics Letters **74**, 1111 (1999).
[9] Z. Z. Guo, X. X. Liang, S. L. Ban, Physica Status Solidi (b)**238**, 173 (2003).
[10] S. Balasubramanian, G. Ceder, K. Kolenbrander, Journal of Applied Physics**79**, 4132 (1996).
[11] C. Van de Walle, Physical Review B**39**, 1871 (1989).
[12] J. Haus, H. S. Zhou, I. Honma, et al, Physical Review B**47**, 1359(1993).
[13] S. Nizamoglu, H. V. Demir, Optics Express**16**, 3515 (2008).
[14] G. Jia, Y. Wang, L. Gong, et al, Digest Journal of Nanomaterials and Biostructures**6**, 43 (2011).
[15] J. Persson, U. Hakanson, M.-J. Johansson, et al, Physical Review B**72**, 085302 (2005).
[16] S.-H. Wei, A. Zunger, Physical Review B**60**, 5404 (1999).

*Corresponding author: jiaguozhi@tcu.edu.cn