

DIELECTRIC MISMATCH EFFECT ON THE ELECTRONIC STATES IN ZnS/CdSe CORE-SHELL QUANTUM DOTS UNDER APPLIED ELECTRIC FIELDS

Ecaterina Cornelia NICULESCU¹, Mihail CRISTEA²

The lowest energy levels of electrons in ZnS/CdSe core-shell quantum dots under applied electric field are studied by using a finite element method. The calculations were performed within the effective mass approximation and taking into account the effect of the mismatch between the dielectric constants of the dot and barrier materials. Several configurations of the nanostructure sizes and electric field strengths have been considered. Our results suggest that the peak emission wavelengths associated with the $2p \rightarrow 1s$ transitions can be adjusted in a desired energy range by changing the structure parameters (dot radius, barrier material) as well as by varying the electric field strength.

Keywords: inverted core-shell quantum dots, dielectric mismatch, optical transitions.

1. Introduction

The advances in the techniques for the semiconductor crystals growth have allowed the fabrication of low dimensional systems like quantum wells, quantum well wires, and quantum dots (QDs). These systems have attracted interest in basic and applied research due to their phenomenology and their potential use to develop optoelectronic devices such as ultrafast optical switches and infrared waveguide devices. Recently core/shell quantum dots (CSQD), i.e. spherical QDs surrounded by a thin second material layer, have been realized [1,2] and theoretically investigated in several works. Feng et al. [3] studied third-order nonlinear optical susceptibilities associated with intersubband transitions in CdSe/ZnS core–shell quantum dots. Nonlinear absorption spectra for intersubband transitions of CdSe/ZnS spherical quantum dots were analyzed by Kostić and Stojanović [4]. In addition, the electronic properties of the hydrogenic impurity in CdSe/ZnS CSQDs surrounded by wide-gap dielectric materials were studied in Ref. [5]. The results suggest that in dielectrically modulated nanodots the donor

¹ Prof., Physics Depart., University POLITEHNICA of Bucharest, România, e-mail: niculescu@physics.pub.ro

² Reader, Physics Depart., University POLITEHNICA of Bucharest, România, Corresponding author e-mail: mcristea@physics.pub.ro

energy can be tuned to a large extent by the structure design, the impurity position and a proper choice of the dielectric media.

Generally, the core material has a narrower bandgap than the shell, but so-called “inverted” core-shell quantum dots in which the shell material has a narrower bandgap than the core have also been obtained [6,7] and studied [8-10]. The dependences of electron energy spectrum and its probability density on nanosystem radius in the spherical anti-dot $ZnS/Cd_xZn_{1-x}S$ have calculated by Holovatsky et al. [8] The work of Tyrrell and Smith [9] has been demonstrated the importance of an accurate description of the nanocrystal valence band structure for the study of the exciton properties in $CdTe/CdSe$ and $CdSe/CdTe$ type-II core-shell nanocrystals. By monitoring radiative recombination lifetimes, Balet et al.[10] reported a continuous transition between type-I and type-II localization regimes in inverted core/shell nanocrystals

Applied external perturbations are useful tools to change the electronic and optical properties of low-dimensional semiconductor structures. In particular, it was proved that the nanostructures under electric fields exhibit some characteristics very different from those of a bulk semiconductor and these effects are more pronouncedly as the carriers’ confinement is decreased. However, because of the increased complexity of the numerical calculations, only a small number of studies related to the electric field effect on the quantum dot with dielectric environment have been done. In a previous work [11] we have investigated the ground state energy and electron cloud localization of the shallow donors in a Si quantum dot under applied electric field taking into account dielectric mismatch with the surrounding matrix. We found that for a freestanding quantum dot the binding energy is strongly enhanced due to the additional interactions of the electron with the polarization charges, whereas this quantity is a decreasing function of the electric field strength. Thus, a control of the energy levels in these structures by tuning the ambient dielectric constant and/or external field can be realized. Recently, [12] we also proved that in core-shell $CdSe/ZnS$ quantum dots covered with a wide-band dielectric material the electric applied field can be used as a valuable parameter which allows a red or blue shift of the threshold energy for the photoionization of the off-center impurities.

In this paper we investigate the electric field effect on the electronic states in $ZnS/CdSe$ inverted core-shell nanodots taking into account the dielectric mismatch between the sphere and the surrounding medium. Calculations have been made within the effective mass approximation by using a finite element method for different configurations of the shell thickness, electric field and dielectric environment. To the best of our knowledge this is the first study on the simultaneous effects of electric field and dielectric confinement on the interlevel transition energies in inverted core-shell nanodots. The paper is organized as follows: in Section 2 is presented the theoretical framework, in Section 3 the

results and discussions are shown, and finally, our conclusions are given in Section 4.

2. Theory

We assume a spherical core (C) with the inner radius R_1 , coated by a spherical shell (S) with R_2 radius, which is further embedded in a dielectric material (Fig. 1). ZnS/CdSe QDs are typically covered with a polymer (polyethylene glycol) [9], so that a band gap energy $E_{g_{matrix}} = 8$ eV and a dielectric constant $\epsilon_{matrix} \cong 2\epsilon_0$ (ϵ_0 being the vacuum permittivity) seem to be reasonable values [9] to represent the organic ligands and external medium. The conduction band profiles of the ZnS/CdSe core-shell QD are modeled using the bulk material parameters. In the numerical calculation we use a conduction band offset of 0.9 eV for the ZnS/CdSe heterointerface [3] and an infinite potential barrier outside of the shell due to the wide-band dielectric which surrounds the nanocrystal.

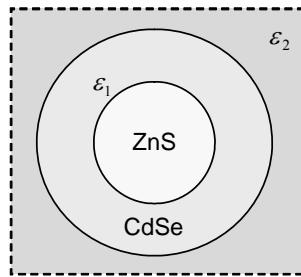


Fig. 1. Schematic of a ZnS/CdSe core-shell quantum dot surrounded by a wide band matrix.

The present theoretical approach uses the envelope-function and parabolic-band approximations [13]. Then, the Hamiltonian for electronic states in a core-shell nanodot under an electric field \vec{F} has the form

$$H = -\frac{\hbar^2}{2} \nabla \left(\frac{1}{m^*(r)} \nabla \right) + U(r) + W(r) + e\vec{F} \cdot \vec{r} \quad (1)$$

Here the first term is the Hermitian kinetic energy operator for a position dependent mass:

$$m^*(r) = \begin{cases} m_{core}, & r \leq R_1; \\ m_{shell}, & R_1 < r \leq R_2. \end{cases} \quad (2)$$

and $U(r)$ represents the step-like confining potential

$$U(r) = \begin{cases} V_0, & r \leq R_1 \\ 0, & R_1 < r \leq R_2, \\ \infty, & r > R_2 \end{cases} \quad (3)$$

The $W(r)$ term in Eq. (1) describes the electron self-polarization potential which originates from the interaction of the electron with its image-charge. For the dielectric constant we assume the same value in the two semiconductors $\epsilon_1 = \sqrt{\epsilon_C \epsilon_S}$ [14], whereas $\epsilon_2 = 2\epsilon_0$ is the dielectric constant of the surrounding matrix.

According to Ref. [15] for this step-like profile with an abrupt change of the dielectric constant at the dot boundaries the self-energy is given by

$$W(r) = \frac{e^2(\epsilon_1 - \epsilon_2)}{8\pi\epsilon_1 R_2} \sum_{k=0}^{\infty} \frac{k+1}{k\epsilon_1 + (k+1)\epsilon_2} \frac{r^{2k}}{R_2^{2k}}. \quad (4)$$

The heterostructures under study are embedded in matrices of lower dielectric constant, $\epsilon_2 < \epsilon_1$. This means that the self-interaction potential is repulsive, so that the quantum confinement due to the barriers potential is amplified by the image-charge presence.

3. Numerical results and discussion

The Schrödinger equation with the Hamiltonian given by Eq. (1) was solved by a finite element method with triangular element and variable step. Calculations were performed by using specialized eigenvalue problem software with nonlinear solver. The solution accuracy was increased by restarting the numerical procedure using as initial value the solution obtained earlier. To ensure a satisfying accuracy of the energy values (about 10^{-3} meV), in the present work the infinite summation in Eq. (4) is truncated to $k_{\max} = 20$. The material parameters used in calculations, taken as in Ref. [3], are given in the Table I.

Numerical calculations were carried out for ZnS/CdSe core-shell nanosystems with a constant inner radius $R_1 = 2$ nm, which is chosen to be slightly larger than the bulk ZnS Bohr radius (≈ 1.5 nm). Two values of the dot radius, $R_2 = 3$ and 5 nm, respectively, are considered.

Table I.

Parameters used in the numerical simulations				
Material	m_e^* / m_0	ϵ / ϵ_0	E_g (eV)	ΔE_c (eV) = V_0
CdSe	0.13	9.3	1.75	0.9
ZnS	0.28	8.1	3.75	

Fig. 2 presents the ground state energy as a function of the applied electric field (EF) for two fixed values of the outer radius taking into account (solid lines) and neglecting (dashed lines) the dielectric confinement effect. For simplicity, we assume the electric field along the z -axis.

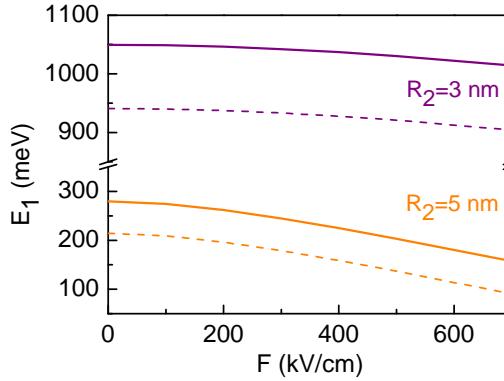


Fig.2. (Color online) Ground state energy as a function of the electric field strength for ZnS/CdSe nanodots taking into account (solid lines) and neglecting (dashed lines) the dielectric confinement effect. The results are for $R_1 = 2$ nm and two values of the outer radius $R_2 = 3$ nm, $R_2 = 5$ nm, respectively.

As a general behavior, the energy monotonically decreases as long as the electric field strength is set to augment [16]. This is because EF pushes the electron against the field direction toward the quantum dot boundary, so that it generates a spatial spreading of the electron wave function. For a given environment, this implies a monotonic diminishing in E_1 , more significantly in large dots due to the decreasing in the degree of carrier confinement. Such a behavior is in accordance with the results plotted in Fig. 3 which shows the cross section of the electron probability density in ZnS/ CdSe QDs with dielectric mismatch at interfaces for different applied electric fields and two outer radii. We observe that for $R_2 = 3$ nm (in the strong confinement regime) at $F = 0$ the electron-wave function is distributed mainly within the core region and its radial symmetry around the dot center is progressively altered by the applied electric field (see Fig. 3A). However, for larger size of the system (Fig. 3B) most of the electron probability density is placed in the shell material. As F increases, the electron wave function loses all symmetries because it is strongly affected by the infinite barriers at $z = -R_2$.

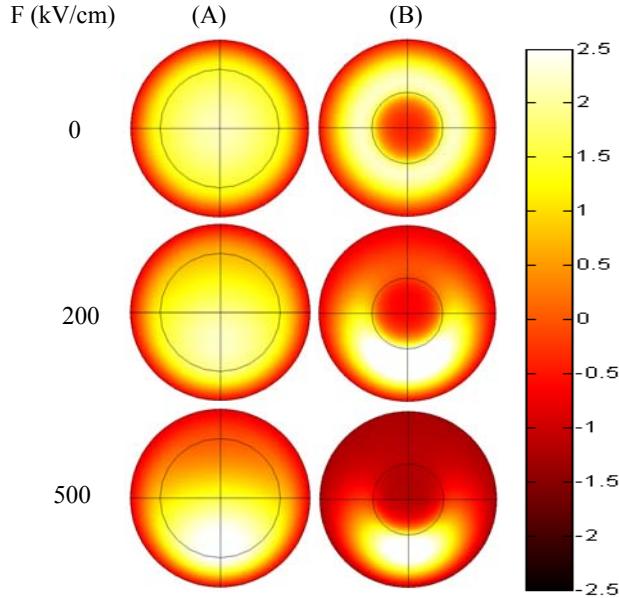


Fig. 3. (Color online) Cross section (at the $y = 0$ plane) of the electron probability density for the ground state in ZnS/CdSe QDs with dielectric mismatch. (A): $R_2 = 3$ nm; (B): $R_2 = 5$ nm. The results are for $R_1 = 2$ nm and different electric field strengths.

Figure 4 shows the energy levels of the $2p$ -like states in ZnS/CdSe QDs as functions of the electric field strength taking into account (solid lines) and neglecting (dashed lines) the dielectric confinement effect.

As expected, the increase in the electric field leads to the splitting of the $2p$ energy level because the radial symmetry of the quantum confinement potential is destroyed. As a consequence, instead of a triple-degenerate state two orthogonal states having different energies are obtained. $2p_0$ -state (blue lines in Fig. 4) exhibits at zero field a probability density having the reflection symmetry with respect to the plane $z = 0$ whereas for the $2p_{\pm}$ -states this quantity is symmetric with respect to the x (y) axis (Fig. 4, red lines). Fig. 4 (a) shows a monotonous increase (decrease) of the $2p_0$ ($2p_{\pm}$) state energy as F enhances, whereas in the case of $R_2 = 5$ nm (Fig. 4(b)) the $2p_0$ -energy reaches a maximum for $F \approx 400$ kV/cm, then it slowly decreases. It is observed that, despite the gain in the excited states energy due to the image charges, the levels splitting exhibits a very weak dependence on the dielectric confinement.

Note also that for $F = 0$ and neglecting the dielectric confinement, the energy levels values are in qualitatively agreement with those reported in Ref. [15] for a ZnS/CdSe cylindrical quantum dot quantum well.

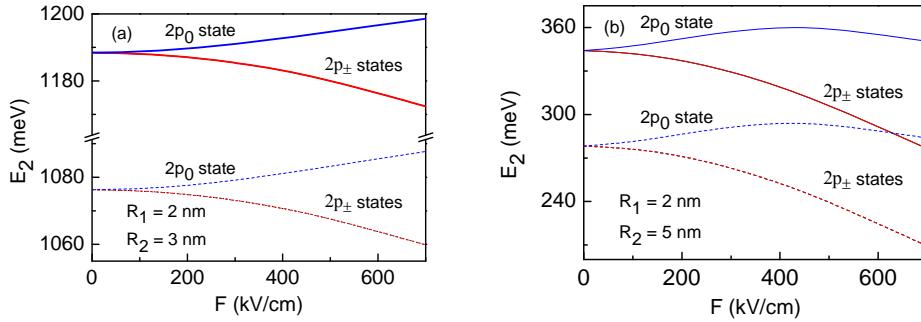


Fig. 4. (Color online) Energy of the 2p-like states vs. the electric field for (a) $R_2 = 3$ nm and (b) $R_2 = 5$ nm. The results are for $\epsilon_2 = 2\epsilon_0$ (solid lines), and $\epsilon_2 = \epsilon_1$ (dashed lines).

The behavior of the electron cloud localization within the structure for 2p-like states is presented in Fig. 5.

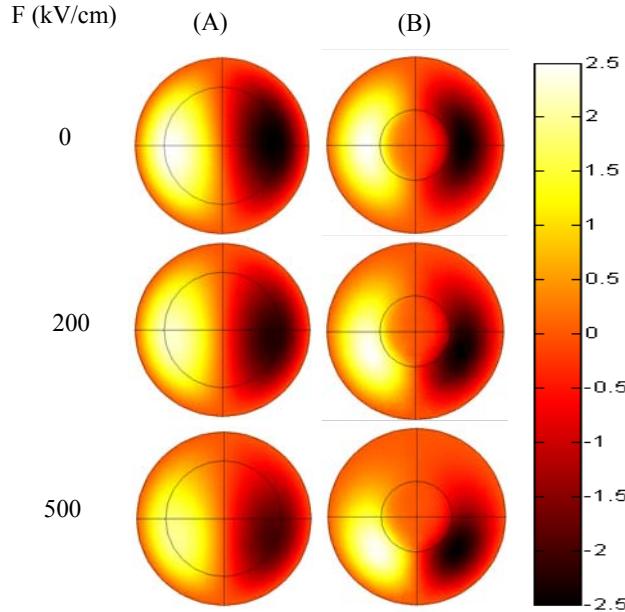


Fig. 5. (Color online) As in Fig. 3 for $2p_{\pm}$ states.

By observing Fig. 5, we notice that for the first excited state the electric field induces a moderate shift of the probability density maximum in the z -direction. This is because in this state the wave function is strongly compressed by the infinite potential barrier. As expected, the change in the electron cloud localization increases as long as the size of the heterostructure augments. For $R_2 = 3$ nm, one observes that the electron wave functions are strongly confined and, as a consequence, the effects of the electric field are minimal. Even for higher values of the field intensity the wave function keeps their symmetry, whereas for an increased outer radius the x-z density of probability shows an obvious displacement against the field direction.

This behavior is in agreement with the electric field dependence of the average distance between the electron and dot center, plotted in Fig. 6.

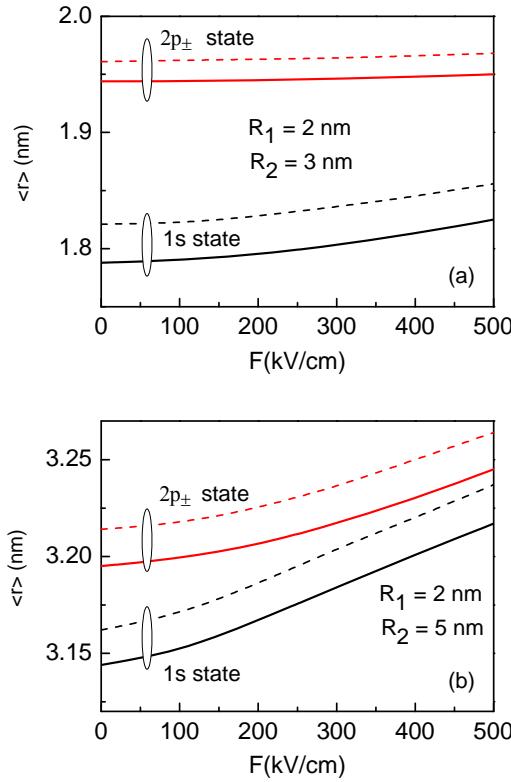


Fig.6. (Color online) The average value of the distance between the electron and dot center for the ground (black lines) and the first excited state (red lines) in a CdSe/ZnS core-shell quantum dot. The results are for: (a) $R_2 = 3$ nm ; (b) $R_2 = 5$ nm and two dielectric constants of the embedding medium: $\epsilon_2 = 2\epsilon_0$ (solid lines), and $\epsilon_2 = \epsilon_1$ (dashed lines).

For small size of the structure (Fig. 6(a)), the electric field effect is partially counteracted by the confining potential and a small increase of $\langle r \rangle$ is observed. On the other hand, in the case of low QD confinement (i. e. large value of the dot radius) the effect of the applied electric field becomes significant (Fig. 6(b)) resulting in a pronounced growing of the wave function extension.

In Fig. 7 we present the calculated wavelength of the lowest optical transitions in ZnS/CdSe core-shell QDs as a function of electric field taking into account (solid lines) and neglecting (dashed lines) the dielectric confinement effect.

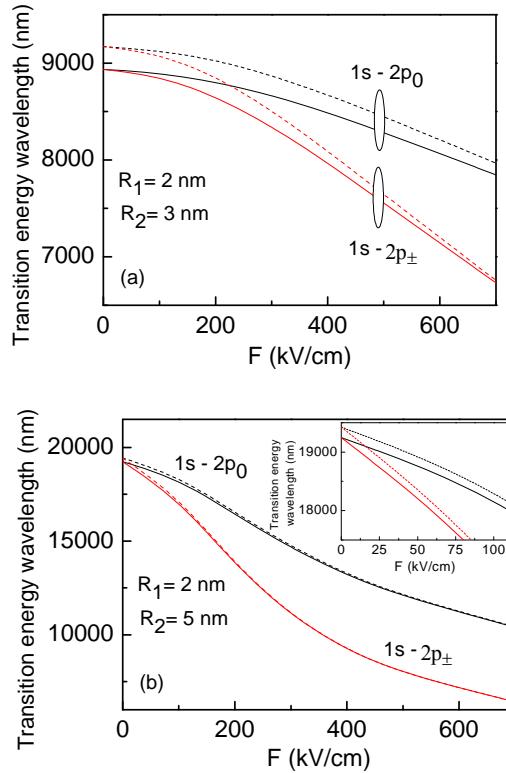


Fig. 7. (Color online) The wavelength of the lowest optical transitions in ZnS/CdSe core-shell QDs as a function of the electric field for (a) $R_2 = 3 \text{ nm}$ and (b) $R_2 = 5 \text{ nm}$. Inset in (b): Zoom for small values of F .

We note that:

- (i) in the regime of small R_2 values, the quantum confinement leads to an increase of the transition energies, more significant when the image-charge effects are taken into account;
- (ii) for nanodots with large sizes the transition energies are less sensitive to the image-charges effect;
- (iii) the electric field effect is more pronounced as outer radius increases due to weaker geometric and dielectric confinements.

4. Conclusions

In this paper, the applied electric field effect on the lowest energy levels in ZnS/CdSe core-shell QDs with dielectric mismatch at interfaces has been investigated. Within the framework of the effective mass approximation, we have shown that the increase of the electric field strength changes the separation between the energy levels and the localization of the electron cloud within the structure. To the best of our knowledge this is the first study on the simultaneous effects of electric field and dielectric confinement on the interlevel transition energies in inverted core-shell nanodots. This control of the optical processes by the external perturbations offers a new degree of freedom in the optoelectronic devices applications.

R E F E R E N C E S

- [1] *F. Q. Chen and D. Gerion*, Nano Lett., **vol. 4**, 2004, pp. 1827
- [2] *X Peng and D Battaglia* Nano Lett., vol. 2, 2002, pp. 1027
- [3] *M. Cristea and E.C. Niculescu*, Eur. Phys. J.B, **vol. 85**, 2012, pp. 91 1-13
- [4] *E.C. Niculescu and M. Cristea*, J. Lumin., **vol. 135**, 2013, pp. 120-129
- [5] *M. Braus, C. Burda and M. A. El-Sayed*, J. Phys. Chem A, **vol. 105** 2001, pp. 5548
- [6] *X. Zhong, R. Xie, Y. Basche, T. Zhang and W. Knoll*, Chem. Mater., **vol. 17**, 2005, pp. 4038
- [7] *V.A. Holovatsky, O.M. Makhanets, and O.M. Voitsekhivska*, Physica E, **vol. 41**, 2009, pp. 1522
- [8] *L. P. Balet, S. A. Ivanov, A. Piryatinski, M. Achermann and V. I. Klimov*, Nano Lett., **vol. 4**, 2004, pp. 1485
- [9] *T.V. Torchynska, J. Douda and R. Peña Sierra*, Phys. Stat. Sol. C, **vol. 6**, 2009, pp. S143-S145.
- [10] *E. J. Tyrrell and J. M. Smith*, Phys. Rev. B, **vol. 84**, 2011, pp. 165328.
- [11] *X. Feng, G. Xiong, X. Zhang and H. Gao*, Physica B, **vol. 383**, 2006, pp. 207-212.
- [12] *P. Harrison*, Quantum Wells, Wires and Dots: Theoretical and Computational Physics of Semiconductor Nanostructures, John Wiley & Sons, 2005
- [13] *S. Hong and J. Singh*, J. Appl. Phys., **vol. 61**, 1987, pp. 5346-5352.
- [14] *C. Delerue and M. Lannoo*, Nanostructures. Theory and Modelling, Springer-Verlag Berlin Heidelberg, 2004.
- [15] *X. Zhang, G. Xiong, X. Feng*, Physica E, vol. **33**, 2006, pp. 120-124.