Research Article

The Excited Electronic States Calculated for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ Quantum Dots Grown by the Sol-Gel Technique

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The present paper is aimed to investigate theoretically the quantum confinement in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ -related quantum dots with x the atomic fraction of Zn. For both electrons and holes, we have calculated the excited bound states with use of the spherical geometry model and assuming a finite potential at the boundary. For electrons, calculations were made by using Bessel function as an orthonormal basis. However, for holes, the confined subbands have been calculated based on squared quantum well envelope wave functions. The subband energies were evaluated for both electrons and holes versus zinc composition as well.

The quantum dots (QDs) are attracting considerable interest in both fundamental and applied research because of their specific properties. In fact, the QDs show a number of striking effects as the quantum confinement, zero-dimensional electronic states, and the nonlinear optical behaviour [1–6]. Among the nanocrystalline II–VI semiconductors, we mention the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$, which has a high potentiality as window layer for solar cells [1, 7–16]. Concerning the epitaxy of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs, there are many growth methods such as the inverted micelles [17], the selective air-growth method technique [18], the single source molecular precursors [19], the colloidal method [20, 21], and the sol-gel technique [1]. In depict of the great interest of QDs based on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$, the existing theoretical works seem to be insufficient to explain all the physical aspects [1]. Most approaches have considered that electrons and holes are confined in a spherical QD of radius R and used an infinite potential barrier model [1, 22–25]. In a recent study, we have investigated the electronic properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs capped inside a dielectric matrix using the sol-gel technique. We, indeed, assumed that both electrons and holes can undergo a quantum confinement in a nanosphere

of radius R but the boundary of the QD is of a finite barrier height [5]. By restricting the study to the ground state for both electrons and holes, we have calculated the shape of the confinement potentials, the quantized energies, their related envelope wave functions and the QDs sizes. It has been established from this study that the confinement energy shows a significant increase with the ZnS molar fraction for both electrons and holes. Moreover, the radius of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs has been found to be decreasing with increased Zn composition. This means that the confinement of carriers increases with composition x . The aim of the present paper is to investigate the electronic structure of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs by using the spherical geometry model. A peculiar attention is paid to the computation of electron and hole excited states. Calculations will be made versus the ZnS molar fraction. The paper is organized as follows: after a brief introduction, we present the theoretical formulation, in then, we report numerical results and discussion. Concluding remarks are summarized in the last part.

The system to model consists of an electron-hole pair confined in a spherical QD of radius R . The nanocrystallite is assumed to be embedded in a dielectric host matrix. It

TABLE 1: Electron band parameters taken from [5] and used to calculate the subband energies.

x	$\frac{m_e^*}{m_0}$	$\frac{m_{hh}^*}{m_0}$	V_e (eV)	V_h (eV)	R (nm)
0.0	0.20	5.00	0.13	0.13	2.0
0.2			0.40	0.10	2.0
0.4			0.40	0.20	1.5
0.6			1.00	1.00	1.5
0.8			1.25	1.00	1.3
1.0	0.28	1.76	1.75	0.60	1.2

TABLE 2: The fit of the subband energies versus composition as calculated for the electron and hole states in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs.

State level	Polynomial law
hh1s	$-0.003x^3 + 0.095x^2 + 0.021x + 0.014$
hh2s	$-0.123x^3 + 0.520x^2 - 0.034x + 0.056$
lh1s	$-1.000x^3 + 1.762x^2 - 0.357x + 0.074$
e-1s	$-0.022x^3 + 0.043x^2 + 0.446x + 0.131$
e-1p	$1.853x^3 - 0.736x^2 - 0.972x + 1.037$

is considered at a temperature T as well, and no external electric field is applied. Electrons and holes have a potential barrier of finite height. On the other hand, the coupling between electron and hole confinements is disregarded. Also, the Coulomb potential associated with the electron-hole interaction has not been taken into account. For the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystal to model, the electronic bound states can be computed using the following equation:

$$\left[-\frac{\hbar^2}{2m_{e,h}^*} \frac{1}{r_{e,h}} \frac{\partial^2}{\partial r_{e,h}^2} r_{e,h} + \frac{\mathbf{L}_{e,h}^2}{2m_{e,h}^* r_{e,h}^2} + V_{e,h}h(r_{e,h} - R) - \varepsilon_{e,h} \right] \psi_{e,h}(r_{e,h}) = 0, \quad (1)$$

where $\hbar$ is the Plank's constant, m^* is the effective mass of the carriers, $\mathbf{L}$ represents the azimuthal momentum operator, V is the height of the confinement potential, $h(t)$ is the step function, ε is the confinement energy, and $\psi(r)$ is the eigen wave function. The subscripts e and h refer to the electron and hole particles, respectively. Equation (1) is derived in the framework of the effective mass theory and in the assumption of the band parabolicity. Taking the eigenfunctions under the form $\psi(r) = (1/r)\varphi(r)Y_l^m(\theta, \varphi)$ where $Y_l^m(\theta, \varphi)$ are the spherical harmonics, (1) may be rewritten as:

$$\left[-\frac{\hbar^2}{2m_{e,h}^*} \frac{d^2}{dr_{e,h}^2} + \frac{l_{e,h}(l_{e,h} + 1)\hbar^2}{2m_{e,h}^* r_{e,h}^2} + V_{e,h}h(r_{e,h} - R) - \varepsilon_{e,h} \right] \varphi_{e,h}(r_{e,h}) = 0. \quad (2)$$

Here, l denotes the quantum number associated with the operator $\mathbf{L}$. The function $\varphi(r)$ is subjected to be equal to zero at the center of the nanosphere. For $l = 0$, that is, the ns states, (2) can be solved using the secular equation of a squared

FIGURE 1: The subbands hh-1s, hh-2s, and lh-1s calculated as a function of Zn composition x in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs. The symbol $\square$ indicates the potential barrier heights for holes.

FIGURE 2: The subbands e-1s and e-1p as calculated versus Zn composition x in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs. The symbol $\square$ indicates the potential barrier heights for electrons.

quantum well in a (θ, φ) direction. For the eigenstates with $l \neq 0$, Bessel functions can be used as an orthonormal basis to solve such an equation. We distinguish two regions: $r < R$ and $r > R$. For the first case, (2) can be rewritten as

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho^2} \right) \right] J_\ell(\rho) = 0 \quad (3)$$

with

$$\rho = k_1 r, \quad k_1 = \sqrt{\frac{2m^*\varepsilon}{\hbar^2}}. \quad (4)$$

Here, $J_\ell(\rho)$ denote the spherical Bessel functions. For $r > R$, using Bessel basis functions, (2) is transformed into

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho^2} \right) \right] J_\ell(\rho) = 0 \quad (5)$$

with

$$\begin{aligned} \rho &= k_2 r, \\ k_2 &= \sqrt{\frac{2m^*(V_{e,h} - \varepsilon)}{\hbar^2}}. \end{aligned} \quad (6)$$

As an adequate approximation to calculate the energy levels of a spherical QD, one can take the asymptotic forms to represent the eigen wave functions:

$$\begin{aligned} J_\ell(\rho) &\approx \frac{\rho^\ell}{(2\ell+1)!!}, \quad r < R, \\ J_\ell(\rho) &\approx \frac{1}{\rho} \sin\left(\rho - \ell\frac{\pi}{2}\right), \quad r > R. \end{aligned} \quad (7)$$

In such a case, the secular equation reads

$$\begin{aligned} &\frac{\ell+1}{\sqrt{(2m_{e,h}^*(V_{e,h} - \varepsilon_{e,h})/\hbar^2)}R} \\ &- \cot g\left(\sqrt{\frac{2m_{e,h}^*(V_{e,h} - \varepsilon_{e,h})}{\hbar^2}}R - \ell\frac{\pi}{2}\right) = 0. \end{aligned} \quad (8)$$

As reported in [5], we have calculated the quantized energies for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs using the spherical model. Calculations were carried out using the squared quantum approach and have been restricted to the ground states (1s) for electrons and heavy holes. In the present work, we attempt to extend these calculations to the excited energy levels, that is, the 2s state for heavy holes, 1s state for light holes, and 1p state for electrons. For holes, we adopt as a basis, the squared quantum well wave functions to express $\varphi(r)$. Thus, the confinement energies as well as the wave functions for the eigenstates ns in nanocrystals are given by

$$\begin{aligned} \tan k_1 R + \frac{k_1}{k_2} &= 0, \\ \psi(r) &= \begin{cases} \frac{A}{r} \sin(k_1 r) Y_0^0(\theta, \varphi), & r \leq R \\ \frac{A}{r} \sin(k_1 R) e^{k_2(R-r)} Y_0^0(\theta, \varphi), & r \geq R \end{cases} \end{aligned} \quad (9)$$

with

$$\begin{aligned} \hbar^2 k_1^2 &= 2m^* \varepsilon, \\ \hbar^2 k_2^2 &= 2m^*(V - \varepsilon) \end{aligned} \quad (10)$$

and A is a normalised factor.

For electrons, we consider Bessel functions under their asymptotic forms as shown in (7). The electron band parameters used in the present work are listed in Table 1.

As reported in [5], these parameters were treated as fitting parameters. As an experimental support, we have used absorption data obtained on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystals grown by sol-gel technique [1]. The fitting consisted of imposing the optical band gap to coincide with the effective band gap calculated for $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs. Values of m_{hh}^* (CdS) and m_{lh}^* (ZnS) are 0.7 and 0.23, respectively, in free electron mass m_0 [26]. For the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs, the effective masses were calculated using Vegard's law. Figure 1 shows the subband energies of the 1s and 2s for heavy holes and 1s for light holes calculated as a function of Zn composition. As shown, the subbands shift up in energy as Zn composition increases going from CdS to ZnS. We have fitted the x -dependence of the hole subbands by using polynomial laws. Analytical expressions obtained are summarized in Table 2. As can be noticed from obtained results (i) the subbands, hh1s, hh2s, and lh1s shift up in energy as Zn composition increases, (ii) opposite to the ground state hh1s, the excited subbands hh2s and lh1s show a more rapid increasing with the increase of the ZnS molar fraction. The change in the confinement property of excited holes is mainly due to the fact that the barrier heights are significantly higher for Zn composition near ZnS compared to that at low zinc contents. In $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QD structures with higher Zn composition, these states, if occupied by photocreated and/or thermal excited holes, can favour the multilevel emissions from the confined subbands. On the other hand, the excited hole states can interact with acceptor impurities intentionally incorporated, governing the transport properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs. For electrons, the relevant values of the 1p state are illustrated versus the Zn molar fraction in Figure 2. It has been found that (i) the excited electron state e-1p is not detected as a localized state in the quantum well up to the composition $x = 0.4$, (ii) this state is, however, not resonant in the Zn composition range $0.6 \leq x \leq 1$ and increases significantly with x . In Figure 2, we have also plotted the confinement energy of the e-1s electron state taken from [5]. Similarly for holes, we have fitted the x -dependent subband energies of the electrons by polynomial laws. The results are reported in Table 2. It is worth noting that energy difference between e-1p and e-1s is particularly higher for Zn composition ranging from 0.8 to 1.0. Such a trend results in the strong increasing of the electron barrier height for higher Zn composition, as reported in [5]. As for holes, the excited e-1p state can influence notably the electrical and optical behaviour of QDs based on the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ ternary alloy.

In summary, we have attempted to calculate the discrete energy spectrum of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ QDs. As a geometry model, we have considered spherical QDs with a finite potential barrier at the boundary. For electrons, we have computed the subband e-1p using Bessel functions. For heavy and light holes, however, we have calculated the subbands hh-2s and lh-1s, respectively. In the latter case, we have adopted the one-dimensional quantum well eigenfunctions. Calculations were extended in all the composition range from CdS to ZnS. In fundamental viewpoint, computation of excited bound states for electrons and holes is of great interest. Indeed, it can provide useful information on many physical properties such as multilevel emission processes, interband transitions,

and transport of charges. In applied physics, this study can open a possible way to design a new class of nanostructure devices. In the near future, we intend to investigate oscillator strengths for both inter- and intra-subband transitions in order to describe the electrooptical behaviour of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ -related QDs.

References

- [1] B. Bhattacharjee, S. K. Mandal, K. Chakrabarti, D. Ganguli, and S. Chaudhuri, "Optical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystallites in sol-gel silica matrix," *Journal of Physics D*, vol. 35, no. 20, pp. 2636–2642, 2002.
- [2] K. K. Nanda, S. N. Sarangi, S. Mohanty, and S. N. Sahu, "Optical properties of CdS nanocrystalline films prepared by a precipitation technique," *Thin Solid Films*, vol. 322, no. 1–2, pp. 21–27, 1998.
- [3] H. Yükselici, P. D. Persans, and T. M. Hayes, "Optical studies of the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystals in borosilicate glass," *Physical Review B*, vol. 52, no. 16, pp. 11763–11772, 1995.
- [4] Y. Kayanuma, "Quantum-size effects of interacting electrons and holes in semiconductor microcrystals with spherical shape," *Physical Review B*, vol. 38, no. 14, pp. 9797–9805, 1988.
- [5] N. Safta, A. Sakly, H. Mejri, and Y. Bouazra, "Electronic and optical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystals," *European Physical Journal B*, vol. 51, no. 1, pp. 75–78, 2006.
- [6] N. Safta, A. Sakly, H. Mejri, and M. A. Zaïdi, "Electronic properties of multi-quantum dot structures in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ alloy semiconductors," *European Physical Journal B*, vol. 53, no. 1, pp. 35–38, 2006.
- [7] V. Alberts, R. Herberholz, T. Walter, and H. W. Schock, "Device characteristics of In-rich CuInSe_2 -based solar cells," *Journal of Physics D*, vol. 30, no. 15, pp. 2156–2162, 1997.
- [8] N. Kohara, T. Negami, M. Nishitani, and T. Wada, "Preparation of device-quality $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ thin films deposited by coevaporation with composition monitor," *Japanese Journal of Applied Physics*, vol. 34, no. 9, pp. L1141–L1144, 1995.
- [9] H. L. Kwok, "A study of ultra-thin $\text{Cu}_x\text{S}-\text{Cd}_y\text{Zn}_{1-y}\text{S}$ polycrystalline solar cells," *Journal of Physics D*, vol. 16, no. 12, pp. 2367–2377, 1983.
- [10] H. S. Kim, H. B. Im, and J. T. Moon, "Effects of cell width on the photovoltaic properties of sintered $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{CdTe}$ solar cells," *Thin Solid Films*, vol. 214, no. 2, pp. 207–212, 1992.
- [11] G. Gordillo, "Photoluminescence and photoconductivity studies on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films," *Solar Energy Materials and Solar Cells*, vol. 25, no. 1–2, pp. 41–49, 1992.
- [12] J. W. Bowron, S. D. Damaskinos, and A. E. Dixon, "Characterization of the anomalous second junction in $\text{Mo}/\text{CuInSe}_2/(\text{CdZn})\text{S}/\text{ITO}$ solar cells," *Solar Cells*, vol. 31, no. 2, pp. 159–169, 1991.
- [13] O. M. Hussain, P. S. Reddy, B. S. Naidu, S. Uthanna, and P. J. Reddy, "Characterization of thin film ZnCdS/CdTe solar cells," *Semiconductor Science and Technology*, vol. 6, no. 7, pp. 690–694, 1991.
- [14] T. L. Chu, S. S. Chu, J. Britt, C. Ferekides, and C. Q. Wu, "Cadmium zinc sulfide films and heterojunctions," *Journal of Applied Physics*, vol. 70, no. 5, pp. 2688–2693, 1991.
- [15] H. H. Gürel, Ö. Akinci, and H. Ünlü, "Tight binding modeling of CdSe/ZnS and CdZnS/CdS II-VI heterostructures for solar cells: role of d-orbitals," *Thin Solid Films*, vol. 516, no. 20, pp. 7098–7104, 2008.
- [16] M. Gunasekaran and M. Ichimura, "Photovoltaic cells based on pulsed electrochemically deposited SnS and photochemically deposited CdS and $\text{Cd}_{1-x}\text{Zn}_x\text{S}$," *Solar Energy Materials and Solar Cells*, vol. 91, no. 9, pp. 774–778, 2007.
- [17] L. Cao, S. Huang, and E. Shulin, "ZnS/CdS/ZnS quantum dot quantum well produced in inverted micelles," *Journal of Colloid and Interface Science*, vol. 273, no. 2, pp. 478–482, 2004.
- [18] H. Kumano, A. Ueta, and I. Suemune, "Modified spontaneous emission properties of CdS quantum dots embedded in novel three-dimensional microcavities," *Physica E*, vol. 13, no. 2–4, pp. 441–445, 2002.
- [19] Y. C. Zhang, W. W. Chen, and X. Ya Hu, "In air synthesis of hexagonal $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles from single-source molecular precursors," *Materials Letters*, vol. 61, no. 26, pp. 4847–4850, 2007.
- [20] K. Tomihira, D. Kim, and M. Nakayama, "Optical properties of ZnS-CdS alloy quantum dots prepared by a colloidal method," *Journal of Luminescence*, vol. 112, no. 1, pp. 131–135, 2005.
- [21] J. Ouyang, M. Vincent, D. Kingston, et al., "Noninjection, one-pot synthesis of photoluminescent colloidal homogeneously alloyed CdSeS quantum dots," *Journal of Physical Chemistry C*, vol. 113, no. 13, pp. 5193–5200, 2009.
- [22] K. K. Nanda, S. N. Sarangi, S. Mohanty, and S. N. Sahu, "Optical properties of CdS nanocrystalline films prepared by a precipitation technique," *Thin Solid Films*, vol. 322, no. 1–2, pp. 21–27, 1998.
- [23] Q. Pang, B. C. Guo, C. L. Yang, et al., " $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ quantum dots: new synthesis and characterization," *Journal of Crystal Growth*, vol. 269, no. 2–4, pp. 213–217, 2004.
- [24] M. C. Klein, F. Hache, D. Ricard, and C. Flytzanis, "Size dependence of electron-phonon coupling in semiconductor nanospheres: the case of CdSe," *Physical Review B*, vol. 42, no. 17, pp. 11123–11132, 1990.
- [25] H. Yükselici, P. D. Persans, and T. M. Hayes, "Optical studies of the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystals in borosilicate glass," *Physical Review B*, vol. 52, no. 16, pp. 11763–11772, 1995.
- [26] W. Ekardt, K. Löscher, and D. Bimberg, "Determination of the analytical and the nonanalytical part of the exchange interaction of InP and GaAs from polariton spectra in intermediate magnetic fields," *Physical Review B*, vol. 20, no. 8, pp. 3303–3314, 1979.