The binding energy of light excitons in spherical quantum dots under hydrostatic pressure

C.A. Moscoso-Moreno, R. Franco, and J. Silva-Valencia
Departamento de Física, Universidad Nacional de Colombia, A.A 5997, Bogotá -Colombia.

Recibido el 18 de diciembre de 2006; aceptado el 9 de abril de 2007

We study the effects of hydrostatic pressure over the ground state binding energy of light hole excitons confined in $GaAs - Ga_{1-x}Al_xAs$ spherical quantum dots. We applied the variational method using $1s$-hydrogenic wavefunctions, in the framework of the effective mass approximation. We computed the exciton binding energy as a function of the dot radius, Al concentrations and pressures. Our results show that (i) the hydrostatic pressure increases the binding energy, for all quantum dot radii; (ii) the binding energy is an increasing function of the Al concentration, for fixed radius and pressure, especially for a smaller dot; (iii) the binding energy follows approximately a linear dependence with the pressure, for fixed radius and Al concentration.

Keywords: Quantum dot; excitons; hydrostatic pressure.

El efecto de la presión hidrostática sobre la energía de enlace de excitones ligeros confinados en puntos cuánticos esféricos de $GaAs - Ga_{1-x}Al_xAs$ es estudiado. Nosotros usamos el método variacional y consideramos funciones de onda hidrogenoides $1s$ bajo la aproximación de la masa efectiva. Se calculó la energía de enlace como función del radio, la concentración de aluminio Al y la presión. Nuestros resultados muestran que (i) la presión hidrostática aumenta la energía de enlace para todos los radios considerados; (ii) la energía de enlace es una función creciente de la concentración de aluminio, para valores fijos del radio y la presión, especialmente para radios pequeños; (iii) la energía de enlace sigue de manera aproximada una dependencia lineal con la presión, para radios y concentraciones de aluminio fijos.

Descriptores: Puntos cuánticos; excitones; presión hidrostática.

PACS: 73.20.Dx; 73.20.Hb; 73.21.La

1. Introduction

The progress in nanoscale technology has made possible the fabrication of quasi-zero-dimensional quantum dots (QDs), the quantum size effects in semiconductor QDs greatly increases highly the electron-hole attraction inside them; in consequence the correlated electron-hole pairs (excitons) remain present even at room temperature. It produces important changes in the optical properties of QDs as compared to those of the corresponding bulk material; the transitions between Wannier excitonic states are an important element linked to those changes [1–4]. In the last few decades, a proper quantitative understanding of the changes in the optical properties of low-dimensional heteroestructures, such as QDs, has been of great interest, due to their importance for potential applications in electronic and optoelectronic devices; theoretical studies predicted that low-dimensional semiconductor heteroestructures would offer the advantage of lower switching energy and enhanced oscillator strength over the confined region, which may be used for application to high-performance devices [5, 9].

Many people have studied the effects of quantization for the excitons in microcrystals or quantum dots; Brus [10] has given a variational calculation for the size dependence of the electron-hole pair state, Nair *et al.* [11] calculated the lowest electron-hole state in semiconductor microcrystals, as a function of their size, using the variational principle with a three-parameter Hylleraas wave function; for very small particles, the Coulomb interaction was treated as a perturbation and they considered an infinite confinement potential.

Kayanuma [12] made a simple variational calculation to find the ground-state energy for an exciton confined in a microcrystal with finite potential barriers. He found that the effect of penetration of the wavefunction outside the microcrystal is quite large in the strong-confinement region, and is consistent with the relatively small blue-shift of the excitation energy observed in CdS microcrystals. Einevoll [13] made a theoretical study of excitons confined in CdS and ZnS QDs, using a single-band effective-mass approximation for the carriers; the confinement potential for the hole and electron were modeled as spherically symmetric potential wells with finite barrier heights, finding a good agreement with experimental data. In the same way J.L. Marin *et al.* [4] used the variational method, and the effective-mass approximation, to calculate the ground-state energy of excitons confined in spherical QDs, with finite height potential walls as a function of the particle radius. They used $1s$-hydrogenic-like wavefunctions for the electron and hole, obtaining a good agreement for a 5-40Åradius with experimental data of CdS, $CdSe$, PbS and $CdTe$ crystallites.

Photoluminescence studies of self-organized InAlAs/AlGaAs quantum dots under pressure were carried out by Phillips *et al.* [6]. The effect of hydrostatic pressure on the optical transitions in self-assembled InAs/GaAs quantum dots was studied by Duque *et al.* [7]. Oyoko *et al.* [8] studied donor impurities in a parallelepiped-shaped GaAs-(Ga,Al)As quantum dot, and they found that the donor binding energy increases with increasing uniaxial stress and decreasing sizes of the quantum dot. Raigoza *et al.* [9] found

the effects of hydrostatic pressure on the exciton states in $GaAs/Ga_{1-x}Al_xAs$ semiconductor quantum wells via a variational procedure, in the frame of the effective-mass and non-degenerate parabolic band approximation; a good agreement with available experimental measurements was obtained. Exciton states in quatum well-wires under electric field and hydrostatic pressure were also studied by this group.

Theoretical research into QDs usually assume the simplification of spherical symmetry for the confinement potential, a geometric situation far from the experimental works in semiconductor QDs, but it makes possible the computations of excitonic contributions for the optical properties; recently M. De Girgio *et al.* [16], found a way to produce spherical QDs using colloidal nanocrystals, thus demonstrating the possibility of their fabrication.

In this paper we present a study of the hydrostatic pressure effect over the binding energy of the ground-state of excitons confined in spherical QDs made of $GaAs$ with $Ga_{1-x}Al_xAs$ barriers for different concentrations of Aluminum $x = 0.15$,0.30,0.45. We use the variational method and the effective mass approach to find the ground-state energy; we take into account the variations with the external applied pressure of the parameters such as dot radius, dielectric constant, confinement potential and effective masses [14,15]. We took a finite confinement potential for the dot. The theoretical method is presented in Sec. 2, the results and the discussion regarding them are shown in Sec. 3; in Sec. 4 we present our conclusions.

2. The Model

In the effective mass approximation, the Hamiltonian of an exciton in a spherical quantum dot of $GaAs-(Ga,Al)As$ under the influence of hydrostatic pressure is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e^*(P)}\nabla_e^2 - \frac{\hbar^2}{2m_h^*(P)}\nabla_h^2 - \frac{e^2}{\varepsilon(P)|\mathbf{r_e}-\mathbf{r_h}|} + V_e(r,P) + V_h(r,P), \quad (1)$$

where $m_e(P)$, $m_h(P)$ are the effective mass of electron and hole respectively, $V_e(r,P)$ and $V_h(r,P)$ are the confinement potentials for the electron and hole, and $\varepsilon(P)$ is the dielectric constant. Note that the above quantities depend explicitly on the hydrostatic pressure. In the Hamiltonian (1), $\mathbf{r_e}, \mathbf{r_h}$ are the distances of the electron and hole with respect to the center of the quantum dot. The confinement potentials for the electron and hole, in the Hamiltonian (1) are given by

$$V_e(r,P)[V_h(r,P)] = \begin{cases} 0, & 0 \le r_e, r_h \le R \\ V_e(P)[V_h(P)] & R \le r_e, r_h \le \infty, \end{cases} \quad (2)$$

where $R = R(P)$ is the radii of the quantum dot, which depends on the hydrostatic pressure.

To solve the Hamiltonian (1), we use a variational approach to approximate the wave functions and eigenvalues implied by the Hamiltonian. Taking into account the spherical confining geometry, the confinement potentials and the Coulomb interaction between the electron and hole, we take the product of 1s-hydrogenic wavefunction as the trial wave function for the exciton [4]. The ground-state wavefunction inside the dot is defined as

$$\psi_i = A\exp[-\alpha(r_e + r_h)](R - \alpha r_e)(R - \alpha r_h), \quad (3)$$

for $0 \le r_e, r_h \le R$. The wavefunction outside the dot is defined as

$$\psi_0 = \frac{B}{r_e r_h}\exp[-\beta(r_e + r_h)], \quad (4)$$

with the condition $R \le r_e, r_h < \infty$. The α and β values are the variational parameters, and the constants A and B are the normalization constants. The boundary condition is

$$\frac{1}{\mu_i^*}\frac{1}{\psi_i}\frac{\partial\psi_i}{\partial r_s}\Big|_{r_s=r_0} = \frac{1}{\mu_o^*}\frac{1}{\psi_o}\frac{\partial\psi_o}{\partial r_s}\Big|_{r_s=r_0}, \quad (5)$$

where s depends on the case of electron or hole and μ_i^*, μ_o^* are the reduced effective mass of the exciton inside and outside the dot. Given the boundary condition, we are able to reduce the two variational parameters to one, having

$$\beta = \frac{q[\alpha r_0(1-\alpha)+\alpha] + \alpha - 1}{r_0(1-\alpha)}, \quad (6)$$

with $q = \mu_o^*/\mu_i^*$.

Hereafter we show the main steps of the variational method so that we can obtain the ground-state energy of the exciton. From the normalization condition of the trial wave function we have

$$\int_{\Omega_i} |\psi_i|^2 d\tau_e d\tau_h + \int_{\Omega_o} |\psi_o|^2 d\tau_e d\tau_h = 1, \quad (7)$$

with Ω_i and Ω_o the volume regions inside and outside the dot, and $d\tau_n$ is the volume element either for the electron (e) or the hole (h). So the normalization constants are given by,

$$A = [I_{N_i}^2 + I_{N_o}^2 f]^{-1/2} \quad (8)$$

and

$$B = Ae^{(-2\alpha-2\beta)R}R^4(1-\alpha)^2, \quad (9)$$

where

$$I_{N_i} = 2\pi\int_0^R e^{-2\alpha u}(R-\alpha u)^2 u^2 du, \quad (10)$$

$$I_{N_o} = \frac{2\pi}{\beta}\exp(-2\beta R), \quad (11)$$

and the constant f is,

$$f = R^8(1-\alpha)^4 e^{-4(\alpha-\beta)R}. \quad (12)$$

The expectation value of the kinetic energy is,

$$\begin{aligned}\overline{K}(P) =& -\langle\psi_i|\frac{\hbar^2}{2m_e^*(P)}\nabla_e^2+\frac{\hbar^2}{2m_h^*(P)}\nabla_h^2|\psi_i\rangle \\ & -\langle\psi_0|\frac{\hbar^2}{2m_e^*(P)}\nabla_e^2+\frac{\hbar^2}{2m_h^*(P)}\nabla_h^2|\psi_0\rangle \\ =& -\frac{A^2}{2\mu_i}I_{N_i}I_{K_i}-\frac{B^2}{2\mu_0}I_{N_o}I_{K_o},\end{aligned} \quad (13)$$

where

$$\begin{aligned}I_{K_i} =& 4\pi\int_0^R (R-\alpha u)e^{-\alpha u} \\ & \times\left\{\left(\frac{2}{u}\frac{d}{du}+\frac{d^2}{du^2}\right)(R-\alpha u)e^{-\alpha u}\right\}u^2du,\end{aligned} \quad (14)$$

and

$$I_{K_o} = 4\pi\int_R^\infty \frac{e^{-\beta u}}{u}\left\{\left(\frac{2}{u}\frac{d}{du}+\frac{d^2}{du^2}\right)\frac{e^{-\beta u}}{u}\right\}u^2du. \quad (15)$$

The expectation value for the confinement potential energy, taking $V_c(P) = V_e(R,P) + V_h(R,P)$, is

$$\overline{V}_c(P) = \langle\psi_o|\hat{V}_c|\psi_o\rangle = \{V_e(P)+V_h(P)\}A^2fI_{N_o}^2. \quad (16)$$

For the Coulomb interaction term we make a spherical harmonic expansion,

$$\begin{aligned}\frac{1}{|\mathbf{r_e}-\mathbf{r_h}|} =& 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y_l^{m*}(\theta_e,\Phi_e) \\ & \times Y_l^m(\theta_h,\Phi_h),\end{aligned} \quad (17)$$

and using this we obtain the expectation value of the Coulomb term, given by

$$\overline{V}_{eh}(P) = -(4\pi)^2A^2J(\alpha,R), \quad (18)$$

with

$$\begin{aligned}J(\alpha,R) =& \int_0^R e^{-2\alpha r_e}(R-\alpha r_e)^2 \\ & \times[F(\alpha,R)+G(\alpha,r_e,R)]r_e^2dr_e,\end{aligned} \quad (19)$$

and

$$F(\alpha,R) = \frac{1}{r_e}\int_0^{r_e} e^{-2\alpha r_h}(R-\alpha r_h)^2r_h^2dr_h \quad (20)$$

$$G(\alpha,r_e,R) = \int_{r_e}^R e^{-2\alpha r_h}(R-\alpha r_h)^2r_hdr_h. \quad (21)$$

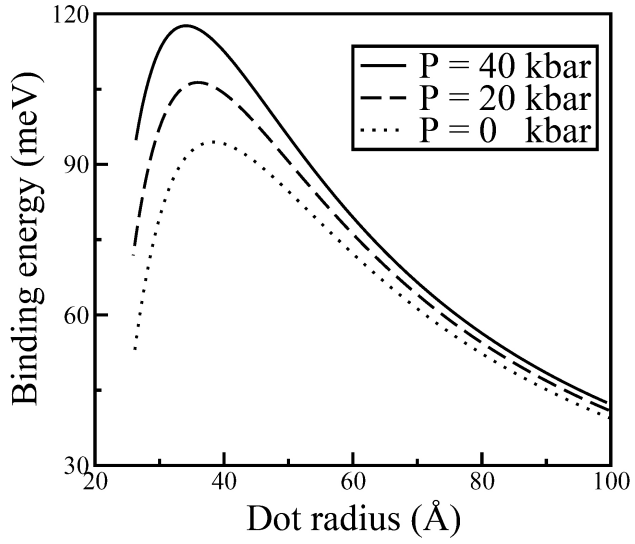

FIGURE 1. Binding energy of an exciton in a $GaAs-(Ga,Al)As$ quantum dot as a function of the dot radius for different pressures.

The ground-state energy for the exciton is now

$$E(\alpha,R,P) = \overline{K}(P)+\overline{V}_{eh}(P)+\overline{V}_c(P), \quad (22)$$

which only depends on the variational parameter, the radius of the quantum dot, and the hydrostatic pressure. We simply need to find the value of α for the ground-state energy to be a minimum, so we set,

$$\frac{\partial E(\alpha,R,P)}{\partial\alpha} = 0. \quad (23)$$

The binding energy for the exciton is defined as the free electron energy E_{elec} plus the free hole energy E_{hole} minus the minimized energy for the exciton:

$$E_{Ex}(R,P) = E_{elec}(P)+E_{hole}(P)-E(\alpha_{min},R,P). \quad (24)$$

The application of hydrostatic pressure modifies the lattice constants, dot size, barrier height, effective masses and dielectric constants. We present the explicit expressions for these quantities as a function of the pressure below, where the pressure is in kbar [14, 15]. The variation of the well width with pressure is given by

$$R(P) = R_0(1-1.5082\times10^{-4}P), \quad (25)$$

where R_0 is the zero pressure width of the quantum dot, taken into account by using $(da/dP) = -2.6694\times10^{-4}a_0$ where a_0 is the lattice constant of $GaAs$. The variation of the dielectric constant with the pressure is given as

$$\varepsilon(P) = 13.13-0.0088P. \quad (26)$$

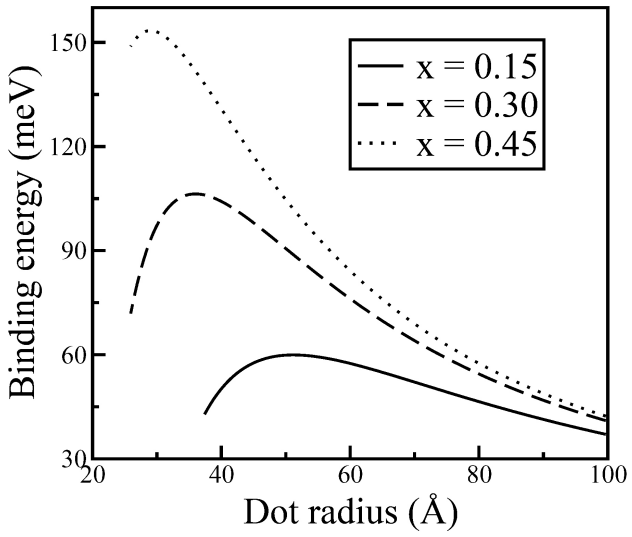

FIGURE 2. Binding energy for the light hole exciton, varying the concentration of Aluminum, for a pressure of 20Kbar.

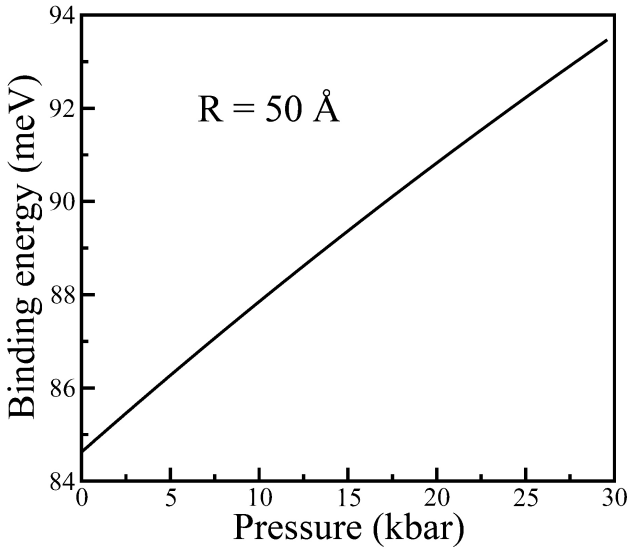

FIGURE 3. Binding energy for the light hole exciton, varying the pressure, for a radius of 50Å.

The effective electron mass in the well and barrier region change as

$$m_e^*(P) = m_e^*(0)\exp(0.0078P); \tag{27}$$

here $m_e^*(0) = 0.067m_{e0}$ is the effective mass without pressure, and m_{e0} is the bare electron mass. We have also chosen the light-hole effective mass as $m_h^*(P) = 0.0951m_{e0}$, independent of the pressure. For simplicity, the dielectric constant, the electron and hole masses were taken to be constant throughout the heterostructure, and equal to the $GaAs$-bulk values.

We assume that the band-gap discontinuity [17, 18] in a $GaAs - Ga_{1-x}Al_xAs$ quantum dot heterostructure is distributed about $40\,\%$ on the valence band and $60\,\%$ on the conduction band with the total band-gap difference $\Delta E_g(x, P)$ (in eV) between $GaAs$ and $Ga_{1-x}Al_xAs$ given as a function of the Al concentration and the hydrostatic pressure P as

$$\Delta E_g(x, P) = \Delta E_g(x) + PD(x), \tag{28}$$

where

$$\Delta E_g(x) = 1.155x + 0.37x^2, \tag{29}$$

is the variation of the energy gap difference without pressure, and $D(x)$ (in eV/kbar) is the pressure coefficient of the band gap given by

$$D(x) = -(1.3 \times 10^{-3})x. \tag{30}$$

Then the height of the potential barrier for electron and holes as a function of Al concentration x and the hydrostatic pressure are given by

$$V_e(P) = 0.6\Delta E_g(x, P), \tag{31}$$

and

$$V_h(P) = 0.4\Delta E_g(x, P). \tag{32}$$

Using these variations the exciton binding energy is obtained for different pressures and dot sizes using the variational method within the effective mass approximation.

3. Results and discussion

In our calculations we consider quantum dots with a radius in a range of 10-100Å and Al concentrations equal to $x = 0.15$,0.30 and 0.45. Although the heavy excitons are more common in experimental results, in this first study we decided to study light-hole excitons because this mass does not depend on the pressure.

The binding energy for a light-hole exciton as a function of the quantum dot radius is shown in Fig. 1 for three different hydrostatic pressure values $P = 0$, $P = 20$ and $P = 40$ kbar, respectively. The behavior of the binding energies without pressure ($P = 0$ kbar) is similar to the previous results found in Refs. 3 and 15. As the pressure is increased, the quantum dot radius and the dielectric constant are reduced. The increasing behavior of the electron effective mass is also well-known. For all pressures we observe that the binding energy increases from its bulk value in $GaAs$ as the dot radius is reduced, reaches a maximum value, and then drops to the bulk value characteristic of the barrier material as the dot radius goes to zero. Note that the binding energy increases with the hydrostatic pressure for any dot radius, reflecting the additional confinement due to the pressure; *i.e.* when the hydrostatic pressure is increased, the exciton becomes more confined and the binding energy increases. Also we observe that the pressure effect is more appreciable for narrow dots, and the maximum position goes to small radius when the pressure increases.

In Fig. 2, we present the binding energy in a spherical $GaAs - Ga_{1-x}Al_x$ quantum dot as a function of the dot radius for different Al concentrations, with hydrostatic pressure fixed and equal to $P = 20$kbar. The Aluminum concentration determines the height of the confinement potential; *i.e.*, low

(high) Aluminum concentration implies a small (high) barrier, therefore the behavior of the binding energy with the Al concentration is important. For all Aluminum concentrations considered in the present work, we observe that the binding energy increases as the radius decreases, reaches a maximum, and then diminishes to a limiting value corresponding to a particular radius of the well for which it is possible to find the free electron and hole energy level. Note that the binding energy increases with the Al concentration reflecting the higher confinement potential, and the maximum binding energy position goes to a small radius when the Aluminum concentration increases. In addition, this plot shows that, for a given Al concentration, the binding energy is very great as compared with the one- and two-dimensional cases, *i.e.* quantum wells and quantum well-wires, respectively.

The dependence of the binding energy on the hydrostatic pressure appears in Fig. 3 for a quantum dot of radii $R = 50$Å. The binding energy shows an approximately linear increase with the pressure; this is in agreement with the results obtained previously in quantum wells [19]. This curve tells us that a system operating under hydrostatic pressure may be used to tune the output of optoelectronic devices without modifying the physical size of the quantum dot. We have not considered pressures beyond 40kbar, because of a direct to indirect bandgap transition for $GaAs$ at about 40kbar [20].

4. Conclusions

We have determinated the ground-state binding energy of excitons inside a GaAs/$Ga_{1-x}Al_xAs$ QD, using the variational method, the effective mass approximation, and considering a hydrogenic-like wavefunction for both electron and holes. We take into account the presence of external hydrostatic pressure and finite confinement potential dependent of the Al concentration. Our results may be resumed thus:

(i) the hydrostatic pressure increases the binding energy for all dot radii,

(ii) the binding energy is an increasing function of the Al concentration for fixed radius and pressure,

(iii) the binding energy approximately follows a linear dependence on the pressure, for a given radius and Al concentration.

We hope that these results will motivate future experimental work in this direction that will confirm our predictions.

Acknowledgments

This work was partially financed by Colombian Agencies COLCIENCIAS (Grant No. 1101-333-18707) and the Universidad Nacional de Colombia (DINAIN-20601003550 and DIB-8003060).

1. T. Takagahara, *Phys. Rev. B* **47** (1993) 4569; *Phys. Rev. B* **60** (1999) 2638; *Phys. Rev. B* **62** (2000) 16840.
2. J.M. Ferreyra and C.R. Proetto, *Phys. Rev. B* **57** (1998) 9061; P.G. Bolcatto and C.R. Proetto, *Phys. Rev. B* **59** (1999) 12487.
3. R.A. Escorcia, R. Robayo, and I.D. Mikhailov, *Phys. Stat. Sol. B* **230** (2002) 431.
4. J.L. Marín, R. Riera, and S.A. Cruz, *J. Phys. Condens. Matter* **10** (1998) 1349.
5. Y. Arakawa and H. Sakaki, *Appl. Phys. Lett.* **40** (1982) 939; H. Temkin, G.J. Dolan, M.B. Panish, and S.N.G. Chu, *Appl. Phys. Lett.* **50** (1987) 413; Y. Arakawa, *Solid-State Electron* **37** (1994) 523.
6. J.D. Phillips, P.K. Bhattacharya, and U.D. Venkateswaran, *Phys. Status Solidi B* **211** (1999) 85.
7. C.A. Duque, N. Porras-Montenegro, Z. Barticevic, M. Pacheco, and L.E. Oliveira, *J. Phys.:Condens. Matter* **18** (2006) 1877.
8. H.O. Oyoko, C.A. Duque, and N. Porras-Montenegro, *J. Appl. Phys.* **90** (2001) 819.
9. N. Raigoza, C.A. Duque, N. Porras-Montenegro, and L.E. Oliveira, *Physica B* **371** (2006) 153.
10. L. Brus, *J. Chem. Phys* **80** (1984) 4403.
11. S. Nair, S. Sinha, and K. Rustagi, *Phys. Rev. B* **35** (1987) 4098.
12. Y. Kayanuma, *Phys. Rev. B* **41** (1990) 10261.
13. G. Einevoll, *Phys. Rev. B.* **45** (1992) 3410.
14. A. Benedictal, B. Sukumar, and K. Navaneethakrishnan, *Phys. Stat. Sol. B* **178** (1993) 167.
15. S.G. Jayam and K. Navaneethakrishnan, *Solid State Communications* **126** (2003) 681.
16. M.D. Giorgio, D. Tari, L. Manna, R. Krahne, and R. Cingolani, *Microelectronics Journal* **36** (2005) 552.
17. R.C. Miller, D.A. Kleinman, and A.C. Gossard, *Phys. Rev. B* **29** (1984) 7085.
18. W. Wang, E.E. Mendez, and F. Stern, *Appl. Phys. Lett.* **45** (1984) 639.
19. N. Raigoza, C.A. Duque, E. Reyes-Gómez, and L.E. Oliveira, *Phys. Stat. Sol. B* **243** (2006) 635.
20. D.J. Wolford and J.A. Bradly, *Solid State Commun*, **53** (1985) 1069.