

Optoelectronic properties of nanosized GaAs

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Received: 30 April 2014, accepted 26 May 2014

Abstract:

Quantum dots (QDs) represent an interesting topic in the controlled modification of optical, electronic and thermoelectric properties of semiconductor materials. Applications in optoelectronic and other devices have been theoretically proposed due to its easy tuning properties by means of controlling size, shape, and density of QDs.

Gallium Arsenide (GaAs) nanostructures are being a popular subject of research since last three decades because of its fascinating properties and potential for nanoelectronic devices which is the trend of miniaturization nowadays. Gallium Arsenide nanoclusters have a significant change of electronic properties from the bulk. This has been the favor in the fabrication of nano-electronic devices for example, optoelectronic devices and transistors. The electronic band structure and optical properties of a GaAs quantum well have been investigated using the pseudopotential approach.

Keywords: *Quantum dot; GaAs; Optical and electronic properties ; pseudopotential method.*

1. Introduction

In recent years, there has been increasing interest in III-V semiconductors as materials for optoelectronic devices [1]. Gallium arsenide (GaAs) is a compound comprising the elements gallium and arsenic. It is a III-V semiconductor, and is used in the manufacture of devices such as microwave frequency integrated circuits, monolithic microwave integrated circuits, infrared light-emitting diodes, laser diodes, solar cells and optical windows. In addition, it is often used as the substrate material for epitaxial growth of other III-V semiconductors, including InGaAs and GaInNAs [1]. It is technologically very important and is the most studied compound semiconductor material [1, 2].

Many of the band structure parameters of bulk GaAs are known with a greater precision than those for any other compound semiconductor ([3] and references therein; [4–9]). However, the new class of materials formed by semiconductor nanostructures has a large and mostly unexplored ensemble of possible applications. The discovery of the nano-solid of various shapes, and its assemblies, has been quite surprising and has thus generated enormous and ever-increasing interest, paving the way for scientific insights and technological thrusts ([10] and references therein). Experimentalists are now able to grow nanostructures of high quality from diverse semiconductor materials [11, 12], with the ability to dope them [13–20]. New physical and chemical properties have been found to occur in such systems, arising from the large fraction of low-coordinated atoms at the surface and the confinement of electrons to a rather small volume [10]. Semiconductor compounds, owing to the tunability of their electronic and optical properties by the three-dimensional confinement of carriers, have attracted considerable interest as technologically important materials. Thus, the

study of quantum confinement in these semiconductors is one of the promising concepts that may lead to a greater understanding of the solid state.

In this paper, we study the electronic and optical properties of nanostructured GaAs in the zinc-blende structure by using the pseudopotential method (PM). The objective of this work is to show the extent to which the quantum confinement effects can modify the electronic and optical properties of bulk GaAs. Although in most cases the PM approach cannot replace the first-principles methods, one must acknowledge a weak connection between state-of-the-art *ab initio* calculations and experimental achievements in the realm of nanostructures [11]. The reason is that nanostructures are small in size, but large in the number of atoms constituting them. Besides, their relevant observables are accessible only through a proper treatment of excitations [11]. Nevertheless, even at the nanoscale the PM has been shown to give accurate results [11, 21]. Moreover, the computational effort needed by this approach is much smaller than that needed by *ab initio* methods.

The paper is organized as follows. Section 2 briefly describes the computational method used in the calculation. The results regarding the effects of quantum confinement on the Optoelectronic properties are presented and discussed in section 3. Finally, the conclusion drawn from the present study is presented in section 4.

2. Computational details

The current calculations are mainly based on the PM (see e.g. [22]). In the PM, the one-electron Schrödinger equation is replaced by a pseudo-wave equation:

$$\left(\frac{p^2}{2m} + V(r)\right) \varphi_k(r) = E_k \varphi_k(r) \quad (1)$$

With $\varphi_k(r)$ denoting the pseudo-wave function and $V(r)$ the pseudopotential. This equation can be used to calculate the physical properties of semiconductors, which are dependent on the valence and conduction electrons only.

The effective potential $V(r)$ is expanded as a Fourier series in reciprocal lattice space. For a binary compound, the expansion is written in two parts, which are symmetric and antisymmetric with respect to an interchange of two atoms about their midpoint. Because of cancellation between the kinetic and potential energies in the vicinity of atomic cores, only a few Fourier terms suffice.

The PM involves the fitting of the atomic form factors $V_A(G)$, which are treated as adjustable parameters, to experiment. Adjustments to the specific pseudopotential form factors, on which the band structure calculation depends, are made using a nonlinear least-squares fitting procedure [23]. More details of the procedure can be found in [24]. In the present work, three band energy level spacings are used for bulk GaAs, namely $r - r$, $r - X$, and $r - L$. The experimental band-gap energies for GaAs at $r - L$ and L high-symmetry points fixed in the fits are 1.42 [25], 1.81 [25] and 1.72 eV [25], respectively. The final adjusted pseudopotential form factors of bulk GaAs are found to be $V_s(3) = -0.239833$, $V_s(8) = 0.0126$, $V_s(11) = 0.059625$, $V_A(3) = 0.060536$, $V_A(4) = 0.05$ and $V_A(11) = 0.01$.

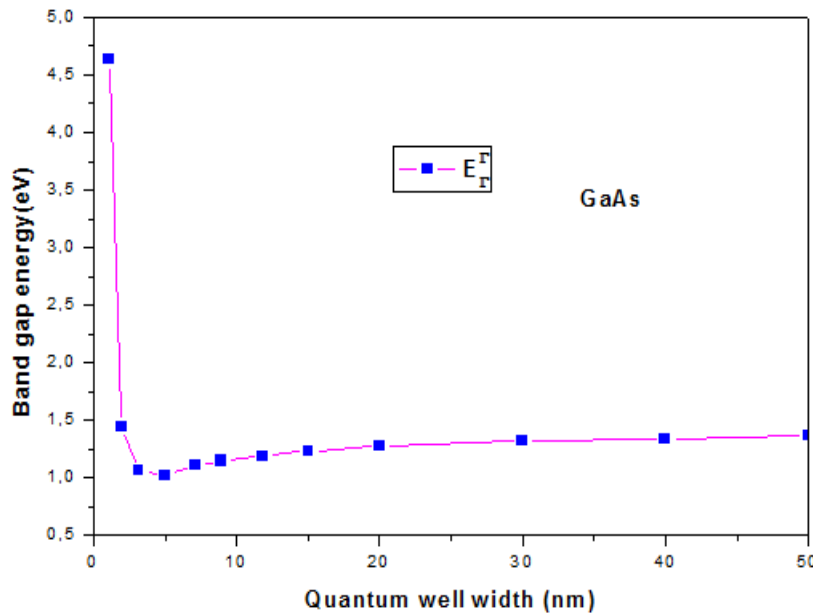


Figure 1. Direct band-gap energy (E_r^T) in nanostructured GaAs as a function of quantum well width

The confinement effect on the energy band gap of a quantum well of width a is calculated using the expression [26, 27]

$$E_g = E_g^0 + \frac{\hbar^2 \pi^2}{2a^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\epsilon a} \quad (2)$$

where E_g is the band gap of the nanostructure, E_g^0 is its corresponding bulk band-gap energy, ϵ is the effective dielectric constant, and m_e^* and m_h^* are the electron and heavy hole effective masses for bulk GaAs, respectively.

By using equation (2), the band-gap energies for GaAs nanostructures at the r , X , and L high-symmetry points in the Brillouin zone have been determined. The results

of calculations are used in the fitting procedure so as to adjust the pseudopotential form factors for each quantum well width a being considered here. The final adjusted pseudopotential form factors for selected quantum well widths of GaAs are given in table 1.

The carrier effective masses m_e^* and m_h^* have been determined for bulk GaAs using a procedure similar to that of Bouarissa [28], where m_e^* and m_h^* are calculated at the r valley in the conduction band minimum and the valence band maximum, respectively.

Table 1. Symmetric ($V_S(G)$) and antisymmetric ($V_A(G)$) pseudopotential form factors for selected quantum well widths of GaAs.

Quantum Wellwidth(nm)	Form factors (Ry)					
	$V_s(3)$	$V_s(8)$	$V_s(11)$	$V_A(3)$	$V_A(4)$	$V_A(11)$
3	-0.084025	0.551957	0.001769	-0.705132	0.05	-0.163124
9	-0.216466	0.0126	0.048521	0.58.086	0.05	0.01
15	-0.228204	0.0126	0.053313	0.072672	0.05	0.01
20	0.231214	0.0126	0.054797	0.069643	0.05	0.01
50	-0.237359	0.0126	0.057940	0.062556	0.05	0.01
100	-0.238903	0.0126	0.058860	0.061441	0.05	0.01

3. Results and discussion

The variation of the direct band-gap energy E_r^r (taken as the transition between the top of the valence band state and the lowest conduction band state at the Brillouin zone centre) as a function of the quantum well width in zinc-blende nanostructured GaAs is shown in figure 1. We observe that as the quantum well width increases from 1 to 3 nm, E_r^r decreases rapidly. Going from a quantum well width of 3 to 5 nm, the decrease becomes weak. Beyond a quantum well width of 5 nm, E_r^r increases slightly and then it becomes almost constant in the well width range 20–50 nm. Thus, the quantum confinement effects are expected to open the band gap when the well width is below 4 nm. The band-gap energy due to a quantum confinement effect becomes much larger than the unconfined or bulk band-gap energy for small quantum well widths (in the well width range 0–2 nm).

The computed electron energy band structures of bulk GaAs (solid curves) and GaAs quantum wells with a well width of 3 nm (dotted curves) along several symmetry points in the Brillouin zone are shown in figure 2. The zero energy reference is taken to be at the top of the valence band for both cases considered here. The valence band maximum is formed by the triply degenerate hybridized Ga(4p,3d)-As(4p)-like orbitals in an antibonding manner. The upper valence bands are derived from the p orbital of As and with some admixture of the p orbital of the cation Ga. The bottom of the valence state is a singlet originating from the bonding Ga(4s)-As(4s)-like orbitals that exhibit a weak dispersion. The As states contribute preferably to the bottom of the valence band, while a substantial number of Ga states contribute to the highest valence band. The behaviour of conduction band states is much more complicated than that of valence band states. The

conduction bands are more delocalized and more ‘free-electron-like’ than the valence bands. The free electron behaviour results in more dispersion bands and band crossing. This trend is generally common for III-V semiconductors [29–31]. The first conduction band at Γ is predominantly of cationic s character. The higher conduction states arise from the hybridization of the Ga(4p,3d)- and As(4p,4d)-like orbitals. For bulk GaAs, the minimum conduction band is at the zone centre Γ . Hence, bulk GaAs is a direct-gap semiconductor as is well known. When moving from the bulk to a GaAs quantum well (nanostructure) with a well width of 3 nm (dotted curves, figure 2), one can note that the electronic band structure is generally affected without changing the shapes of the bands. Practically all the bands are shifted. The shift is not constant and depends on the k -point and energy. The L -point conduction-band minimum moves down relative to the valence-band maximum in such a way that the lowest conduction band occurs at the L high-symmetry point instead of Γ (in the case of bulk GaAs). Therefore, nanostructured GaAs becomes an indirect (Γ - L) band-gap semiconductor. The bottom of the valence state in the case of nanostructured GaAs is shifted upwards, thus suggesting a de-enhancement of the full valence band width. This in turn is an indication of the change in the crystal ionicity when moving from bulk to nanostructured GaAs. It has been reported in the literature that the antisymmetric gap (the gap between the first and the second valence bands at the X point) is related to the ionicity of the semiconductor [32, 33] in such a way that it grows with increasing ionicity. As can be seen from figure 2, when moving from bulk to nanostructured GaAs, this gap decreases, thus suggesting the decrease in ionicity of GaAs. Based on quantum confinement theory [10], the effect of quantum confinement on the electronic properties may be explained as due to the Coulomb potential and kinetic energies of electron-hole pairs (usually called excitons),

which are responsible for the photoluminescence blueshift of nanometric semiconductor; the photoluminescence blueshift is dictated by the joint effect of the intrinsic band gap expansion and electron-phonon coupling. On the other hand, the higher-conduction states are also affected when moving to the

nanometric scale. This is an indication of the change in the transport properties when one goes from bulk to nanostructured GaAs. The effect of quantum confinement on the transport properties can be traced back to the confinement of the charge carriers, which results in a change in the carrier's effective masses.

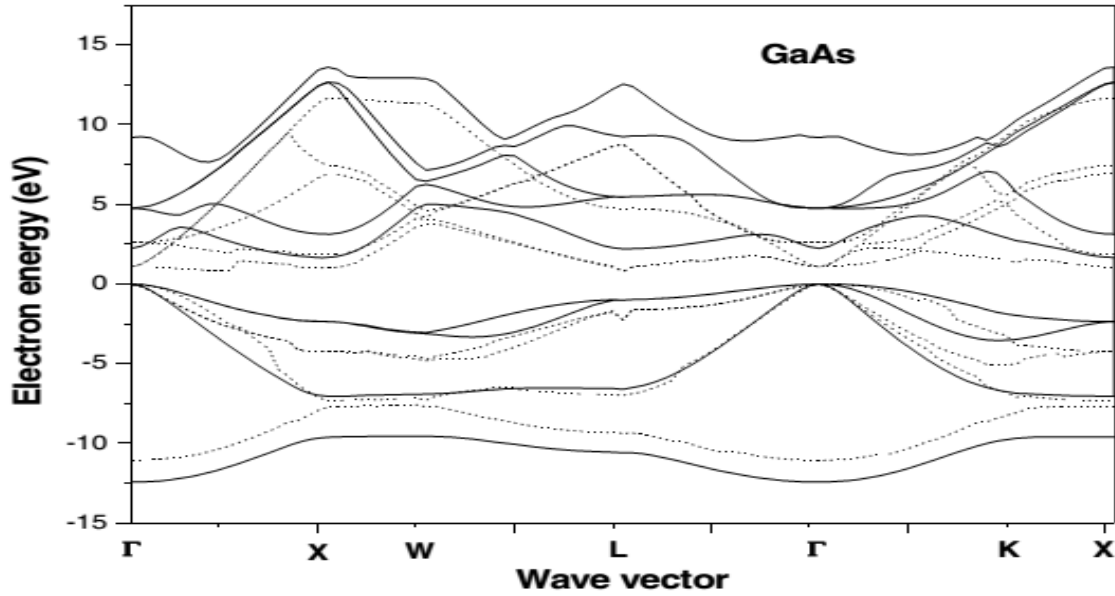


Figure 2. Electronic band structures for bulk GaAs (solid curves) and GaAs quantum wells with a quantum well width of 3 nm (dotted curves).

The study of dielectric properties is concerned with the storage and dissipation of electric and magnetic energy in materials. It is important to explain various phenomena in electronics, optics and solid-state physics. The transverse effective charge e_T^* is a basic parameter characterizing the dielectric properties of solids. Its value is dynamic and reflects the effects of covalency with respect to some reference ionic value [34]. The definition of the charge depends critically on what physical quantity is assumed to be measured. In this paper, e_T^* has been calculated using a relation similar to that used previously in [29], i.e.

$$e_T^* = \frac{\Delta z}{2} + \frac{4\alpha_p}{1+\alpha_p^2} \quad (3)$$

In our case, $\Delta z = -z_{Ga} + z_{As}$, where z are the valences. The variation in e_T^* as a function of GaAs quantum well width is depicted in figure 3. From an inspection of this figure, one can note that with increasing the quantum well width up to 50 nm, e_T^* decreases rapidly. However, when the quantum well width goes beyond the value of 50 nm up to 100 nm, the de-enhancement of e_T^* becomes slow and it tends to be constant. This suggests that e_T^* in nanostructured GaAs is larger than that in bulk GaAs. We may then conclude that the effect of confinement in GaAs leads to an increase in e_T^* .

The dielectric constant is an essential piece of information when designing capacitors and in other circumstances where a material might be expected to introduce capacitance into a circuit. In polar materials atomic displacements create dipoles. The long-range macroscopic electric field accompanying these displacements is determined by a non-analytical contribution to the dynamical matrix [35, 36], consisting of the tensors of the Born effective charges and of the high-frequency dielectric constants. Nevertheless, in the zinc-blende structure (like in our case here), those tensors are isotropic [37, 38]. Thus, the high-frequency dielectric constant (ϵ_∞) is a scalar and can be derived from the expression

$$(\epsilon_\infty = n^2) \quad (4)$$

where n is the refractive index. The latter has been calculated using the Ravindra et al [39] model

$$n = \alpha + \beta E_g \quad (5)$$

where E_g is the fundamental energy band gap, $\alpha = 4.084$ and $\beta = -0.62 \text{ eV}^{-1}$. The model has been chosen because it is found to show better agreement with the known data for n in III-V semiconductors [40]. The dependence of ϵ_∞ on the GaAs quantum well width is shown in figure 4. We observe that ϵ_∞ decreases monotonically and nonlinearly with increasing

the quantum well width up to 100 nm. Since materials with high-dielectric constants are useful in the manufacture of high-value capacitors, the behaviour of ϵ_∞ with respect to the quantum well width suggests an enhancement in the ability of nanostructured GaAs to

store electrical potential energy under the influence of an electric field. In other words, the dielectric capacity of nanostructured GaAs becomes stronger and hence the material becomes a good insulator.

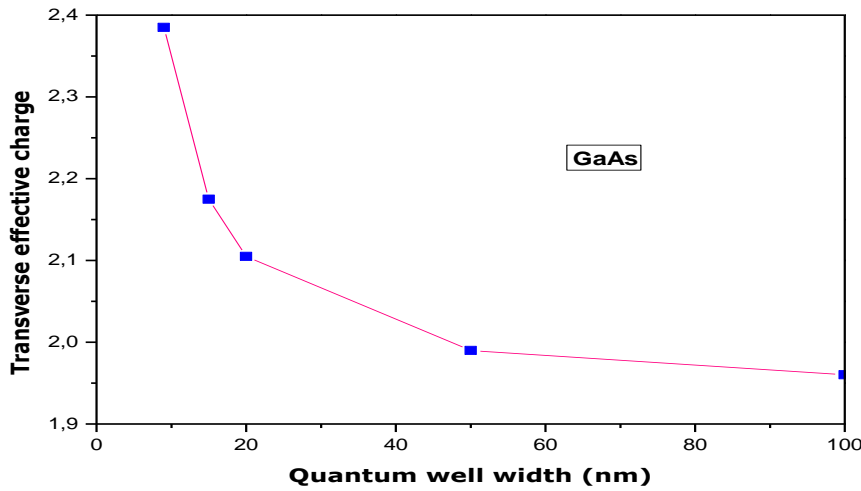


Figure 3. Transverse effective charge in nanostructured GaAs as a function of quantum well width

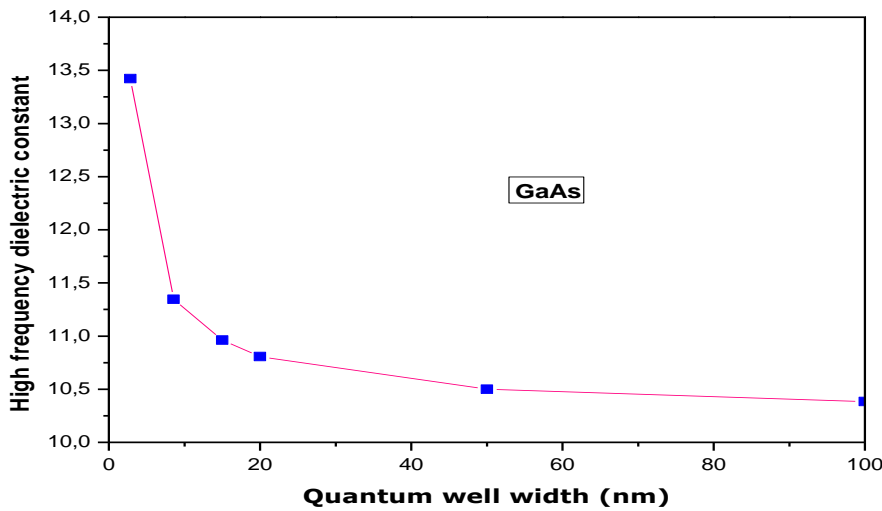


Figure 4. High-frequency dielectric constant in nanostructured GaAs as a function of quantum well width.

The calculations are extended to include the static dielectric constant (ϵ_0).

In this respect, ϵ_0 has been determined using the relation that holds between ϵ_0 and ϵ_∞ [41],

$$\frac{\epsilon_0 - 1}{\epsilon_\infty - 1} = 1 + v \tag{6}$$

where v is given by

$$v = \frac{\alpha_p^2 (1 + 2\alpha_c^2)}{2\alpha_c^4} \tag{7}$$

and α_p is the polarity that was obtained using the Vogl definition [42]

$$\alpha_p = -\frac{V_A(3)}{V_S(3)} \tag{8}$$

Here, $V_S(3)$ and $V_A(3)$ are the symmetric and antisymmetric pseudopotential form factors at G(111), respectively, whereas α_c is the covalency of the material in question that was estimated from the relation

$$\alpha_c = \sqrt{1 - \alpha_p^2} \tag{9}$$

In figure 5, ϵ_0 is plotted against the GaAs quantum well width. Note that ϵ_0 decreases monotonically with increasing the quantum well width. The trend of ϵ_0 seems to be similar to that of ϵ_∞ . Both trends indicate the enhancement of the ability of nanostructured GaAs to store electrical potential energy under the influence of an electric field. On the other hand, it should be

mentioned that for a quantum well width of 100 nm, the value of ϵ_0 is found to be 11.40. This is consistent with the fact that ϵ_0 for bulk GaAs is 11.21 (according to our results) and with the behaviour of ϵ_0 , which shows a decrease with increasing the quantum well width, i.e. beyond a quantum well width of 100 nm, ϵ_0 goes from 11.40 (nanostructured GaAs) to 11.21 (bulk GaAs).

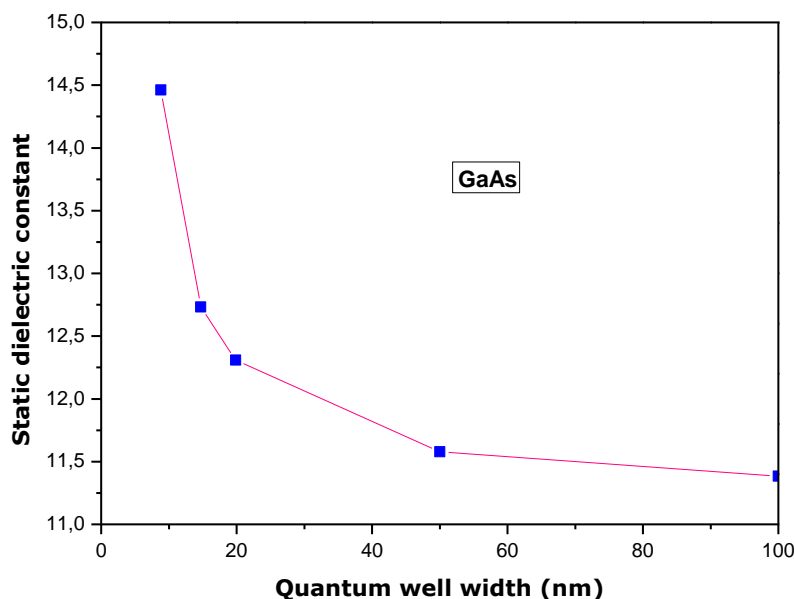


Figure 5. Static dielectric constant in nanostructured GaAs as a function of quantum well width.

4. Conclusion

Based on the pseudopotential approach, the effect of quantum confinement on electronic and optical properties of a GaAs quantum well has been investigated. The quantum well width was taken to be in the range 1-100 nm. The direct band-gap energy E_g^r was found to vary non-monotonically with the quantum well width. An inspection of the electronic band structure showed that quantum confinement has an important effect on the electronic and transport properties. In addition, for a quantum well width of 3 nm, it is found that nanostructured GaAs becomes an indirect ($r-L$) band-gap semiconductor. As far as the dielectric properties are concerned, our results showed that the effect of confinement in GaAs leads to an increase in the transverse effective charge, high-frequency dielectric constant and static dielectric constant, thus indicating that the dielectric capacity of nanostructured GaAs becomes stronger and hence the material of interest becomes a good insulator. The present study may help in the discovery of new desired properties when moving from bulk to nanostructured GaAs.

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