Nano-Scale core effects on electronic structure properties of gallium arsenide

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Abstract

Ab – initio density function theory (DFT) calculations coupled with Large Unit Cell (LUC) method were carried out to evaluate the electronic structure properties of III-V zinc blend (GaAs). The nano – scale that have dimension (1.56-2.04)nm. The Gaussian 03 computational packages has been employed through out this study to compute the electronic properties include lattice constant, energy gap, valence and conduction band width, total energy, cohesive energy and density of state etc. Results show that the total energy and energy gap are decreasing with increase the size of nano crystal . Results revealed that electronic properties converge to some limit as the size of LUC increase .

تأثير حجم اللب على الخواص الالكترونية للكاليوم – ارسيناید

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الخلاصة

باستخدام حسابات ميكانيك الكم وفق نموذج الحساب التام وفق نظرية دوال الكثافة (DFT) مع طريقة (LUC) . تم حساب الخواص الالكترونية للكاليوم ارسيناید (GaAs) ذو التركيب البلوري III-V Zinc blend ولابعاد اللب تتراوح بين (2.04- 1.56) نانومتر وذلك باستخدام برنامج 03 Gaussian حيث اخذ بنظر الاعتبار خواص ثابت الشبيكة وفجوة الطاقة وعرض كل من حزمة التكافؤ والتوصيل والطاقة الكلية وطاقة الترابط و كثافة المستويات ..الخ . وبينت الحسابات تناقص كل من فجوة الطاقة والطاقة الكلية مع زيادة حجم اللب وان الخواص الالكترونية تقترب مع زيادة حجم (LUC).

Introduction

Gallium Arsenide (GaAs) is the most technologically important and the most studied compound semiconductor material. Many band structure parameters for GaAs are known with a greater precision than for any other compound semiconductor. This is especially true of the fundamental energy gap with a value of 1.519 eV [1]. Gallium arsenide has been intensively investigated in recent years. Particular properties studied is direct band gap for photonic application [2] , Nanotube [3] and its internally – carrier transport and higher mobility for generating microwaves [4] . Calculation of the Nano – structure properties such as lattice constant, cohesive energy play an important role in the physics of condensed matter. Theoretical studies of properties continue to be great importance. Among these are semiemperical and Ab- initio. The extension made use the large unit cell method to important periodic boundary condition (PBC) of solid. Previous LUC – INDO calculation for semiconductor had focused on diamond and silicon [5, 6]. We shall use density function theory at the

generalized gradient approximation level (Perdew , Burke , and Emzerhof PBE approximation) coupled with Large unit cell method (LUC-DFT) to evaluate the electronic structure of GaAs which is a well developed theory that had been applied repeatedly for the nanocrystals electronic structure [7] .

Theory

The basic idea of Large uint cell (LUC) is in computing the electronic structure of the unit cell extended in a special manner at k=0 in the reduced Brillion Zone . This equivalent to a band structure calculation at those k-point , which transform to Brillion Zone center on extending the unit cell . Using linear combination of atomic orbitals (LCAO) , the crystal wave function use the density functional theory at the generalized gradient approximation method level [7].

Kohn-Sham density theory [8, 9] is widely used for self consistent − field electronic structure calculations of the ground state properties of atoms, molecules, and solids. In this theory, only exchange − correlation energy $E_{XC} = E_X + E_C$ as a functional of the electron spin densities $n_\uparrow(r)$ and $n_\downarrow(r)$ must be approximated

The local spin density (LSD) approximation:

$$E_{XC}^{LSD}[n_\uparrow, n_\downarrow] = \int d^3 r \ n \in_{XC}^{unif} (n_\uparrow, n_\downarrow) \qquad (1)$$

where $n = n_\uparrow + n_\downarrow$, and the generalized gradient approximation (GGA)

$$E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int d^3 r \ f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) \qquad (2)$$

In comparison with LSD, GGA's tend to improve total energy, atomization energies, energy barriers and structural energy differences.

To facilitate particle calculations, $\in_{XC}^{unif}$ and f must be parameterized analytic

functions. The exchange-correlation energy per particle of a uniform electron gas, $E_{XC}^{LSD}(n_\uparrow, n_\downarrow)$, is well established [9], but the best choice for $f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$ is still a matter of debate.

Figs. (1 and 2) show the final geometrically optimized nanocrystal using density functional theory (DFT) at the B3LYP level (Becke, three-parameter, Lee–Yang–Parr) using STO-3G basis states.

The geometrical optimization calculations are performed with simultaneous optimization and complete convergence of maximum displacements, root mean square (RMS) displacements, maximum forces and RMS forces of all atoms in the nanocrystal. As an example, RMS forces are optimized to less than 0.0003 Hartree/Bohr which is the standard convergence limit of Gaussian03 program [10]
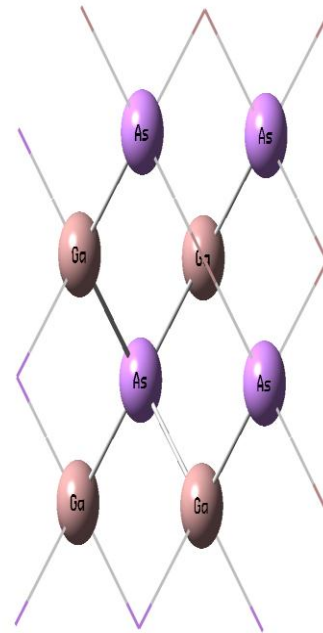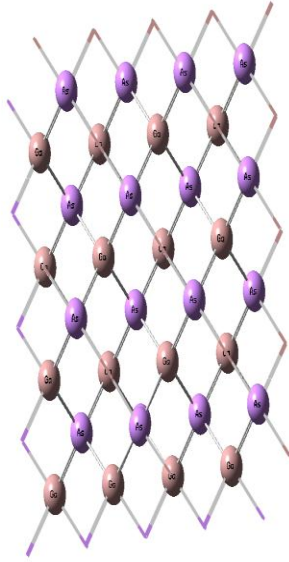

Fig.(1): GaAs 8 atoms core LUC

Fig.(2): GaAs 64 atoms core LUC

Results and Discussions

Figs.(3 and 4) show the lattice constant optimization of 8 and 64 atom core LUC as a function of total energy respectively, while the equilibrium lattice constant occurred at a point in which the attraction forces between the atoms equals to the repulsion forces [11]. Based on the total energy results, we obtained the cohesive energy (Ecoh) as follows: $E_{coh}=E_{tot}/n8-E_{free}-E_0$. Here, E_{tot} is the total energy, where n is the number of core atom, E_{free} is the free atom sp shell energy, and E_0 is the zero − point vibration energy. The cohesive energy is corrected for the zero-point motion of the nuclei. This correction is due to the fact that unlike the classical harmonic oscillator, the vibrational ground state is not equal to zero but equal to $E_0= 0.067$ eV, is calculated by the formula $E_0= (9/8)\, k_B\theta_D$ (per atom) [12], where k_B is Boltzmann constant, with θ_D being the Debye temperature which is equal to 360 K [13]. The results of cohesive energies as a function of lattice constant are obtained by the above method at zero temperature. Figures (5 and 6) display the cohesive energy versus lattice constant of GaAs obtained using the same set of parameters.

Figs. (7 and 8) show the variation of the total energy and energy gap with the variation of the number of core atoms; it is shown that the total energy and energy gap for core part decreases with increasing the number of atoms per LUC. On the scale shown in this figure, the size dependence of the energy is linear. The total energy has a high sensitivity to the potential energy of the crystal. The potential energy of the crystal varies with all the afore-mentioned effects [14]. While the variation of both valence and conduction band widths with the variation of the number of core atoms are shown in Fig.(9). the valence band width is shown to increase with increasing number of atom per LUC, because of the geometry effects on electronic structure of nanocrystals. At the convergence pla-teau Bravais cubic lattices seem to have higher valence band width. That parallelepiped cells have less gap values than cubic ones [14]. Density of states of core 8 and 64 atoms LUC as a function of energy levels are shown in Fig(10 and11) .
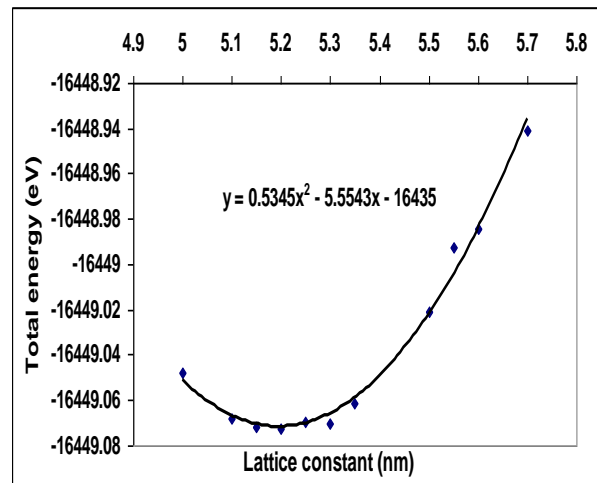

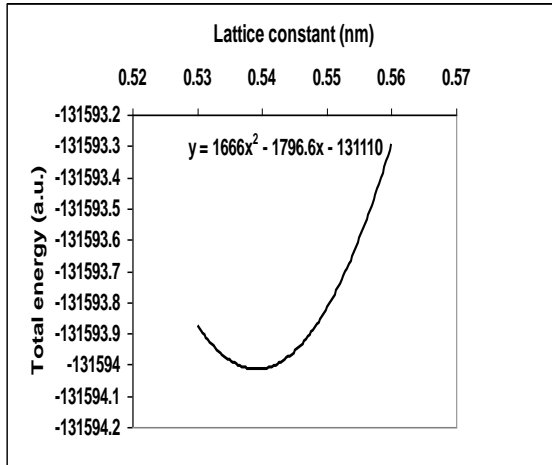*Fig.(3) : Total energy of 8 atoms of GaAs nanocrystal core as a function of lattice constant*

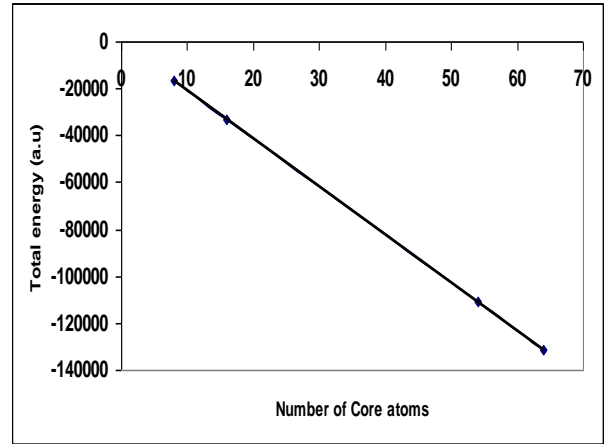*Fig.(4) : Total energy of 64 atoms of GaAs nanocrystal core as a function of lattice constant*

Fig.(5) : Cohesive energy of 8 atoms of GaAs nanocrystal core as a function of lattice constant

Fig.(6) : Cohesive energy of 64 atoms of GaAs nanocrystal core as a function of lattice constant

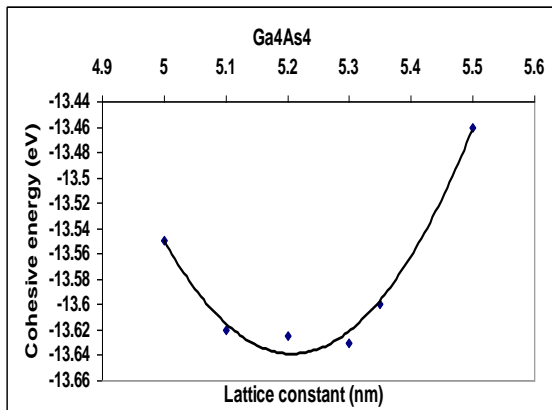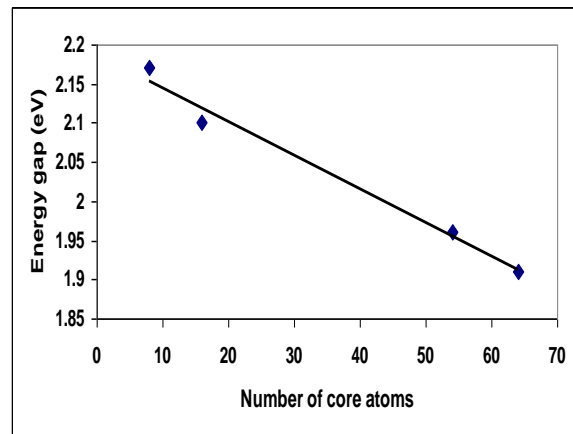*Fig.(7) : Total energy of GaAs nanocrystals as a function of the number of core atoms*

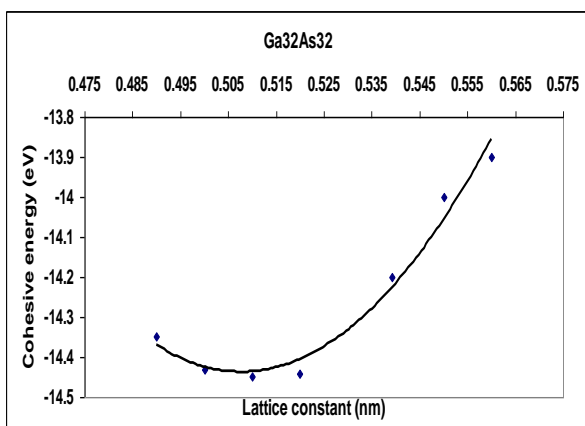*Fig.(8) : Energy gap of the core part of GaAs nanocrystals as a function of the number of core atoms*
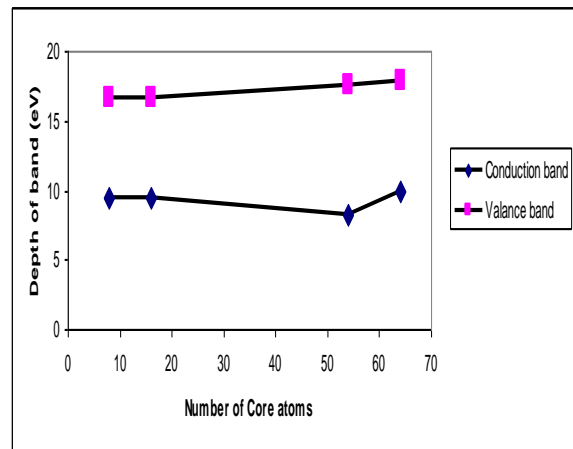

Fig.(9) : Valence and conduction bands variation with lattice constant of GaAs nanocrystals

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Fig. (10): Density of states of 8 Core atoms of core part of GaAs . Valence band are shown with bold lines while conduction band are shown with ordinary lines. The energy gap is shown between the two bands. (Eg=2.2 eV)
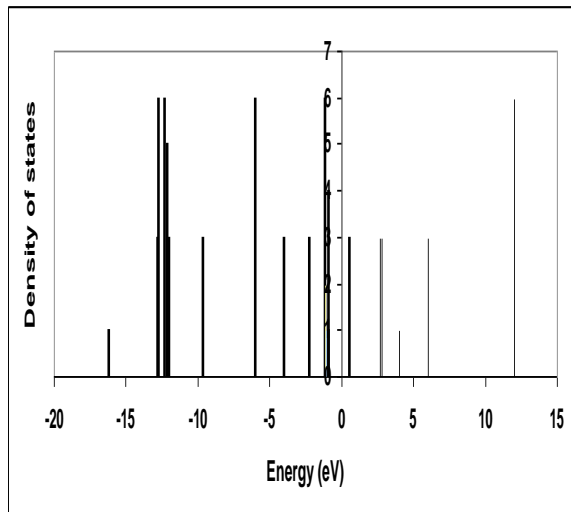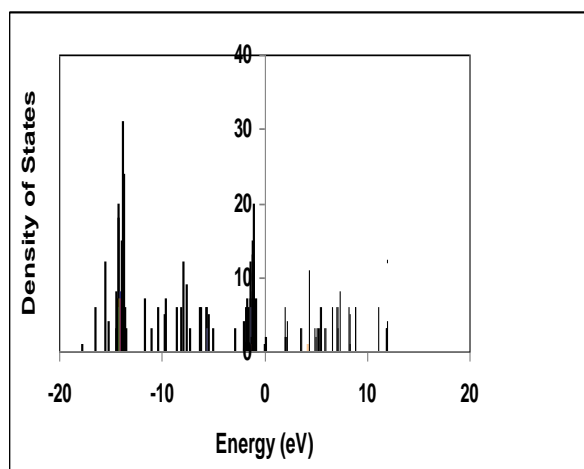

Fig. (11): Density of states of 64 Core atoms of core part of GaAs . Valence band are shown with bold lines while conduction band are shown with ordinary lines. The energy gap is shown between the two bands. (Eg=1.85 eV)

Conclusions

The obtained results show that total energy and energy gap decreasing with increase number of core atoms, but valence band increase with increase number of core atoms because of the geometry effects on electronic structure of nanocrystals. It is found that the equilibrium lattice constant and cohesive energy are in reasonable agreement with experimental result. The degenerate of state increase with number of core.

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