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Study of the electronic structure of indium gallium phosphide $In_{0.5}Ga_{0.5}P$ nanocrystals

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Abstract

The electronic structure of zinc blend indium gallium phosphide $In_{0.5}Ga_{0.5}P$ nanocrystals which have dimension (2-2.8 nm) is investigated using the density functional theory coupled with large unit cell (LUC) for the different size core (8 ,16,54,64) atoms respectively. The investigated properties include total energy, energy gap, conduction band, valence band, cohesive energy, ionicity and density of state etc. as a function of core size and lattice constant. Results show the shape effect of increasing the core size and lattice constant on these electronic properties.

Key words

Electronic structure, InGaP nanocrystalsl.

Article info

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دراسة الخواص الالكترونية النانوية للانديوم – كاليوم – فوسفايد

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الخلاصة

تمت دراسة التركيب الالكتروني لبلورات الانديوم – كاليوم – فوسفايد ($In_{0.5}Ga_{0.5}P$) ذات الابعاد مابين (2-2.8) نانومتر باستخدام نظرية دوال الكثافة (DFT) مع طريقة (LUC) لمنطقة اللب(8، 16، 54، 64) ذرة على التوالي . ان الخواص التي تم بحثها تضمنت الطاقة الكلية ، فجوة الطاقة ، حزمتي التكافؤ والتوصيل ، طاقة الترابط وكثافة المستويات مع حجم اللب وثابت الشبيكة . النتائج بينت تأثير الشكل بسبب زيادة حجم اللب مع ثابت الشبيكة على هذه الخواص الالكترونية .

Introduction

InGaP is a semiconductor composed of indium, gallium and phosphorus. It is used in high-power and high-frequency electronics because of its superior electron velocity with respect to the more common semiconductors silicon and gallium arsenide[1]. It is used mainly in high electron mobility transistor (HEMT) and heterojunction bipolar transistors (HBT) and it has attracted many attentions in high speed and power applications due to the superior transport properties [2], it is also used for the fabrication of high efficiency solar cell used for space applications and, in combination with alumimium (AlInGaP alloy) to make high brightness laser emission diode with orange-red, orange, yellow, and green colors. $Ga_{0.5}In_{0.5}P$ is used as the high energy junction on double and triple junction photovoltaic cells grown on GaAs [3]. Growth of GaInP by epitaxy can be complicated by the tendency of GaInP to grow as an ordered material, rather than a truly random alloy. This changes the band gap and the electronic and optical properties of the material [4]. The InGaP ternary alloy is an attractive material for the preparation of a variety of optoelectronic and microelectronic devices.. Precise design of these devices requires the knowledge of basic material parameters, such as the band gap energy (Eg) [5].

The large unit cell (LUC) method is used for the simulation of the band structure for several kinds of bulk materials including diamond and zinc blend structured materials [6-10]. Density functional theory is widely used for self – consistent – field electronic structure calculations of the ground – state properties of atoms, molecules and solids[11]. The aim of this work is to study the electronic structure properties for InGaP nanocrystals which are used in electronic devices.

Theory

Density functional theory (DFT) coupled with the large unit cell (LUC) were used in the evaluation of the electronic structure of InGaP nanocrystals using Hartree-Fock ab-initio method. The Large unit cell (LUC) gives the profits gained from cyclic boundary in simulating the solid . The LUC alters the shape and the size of the primitive unit cell so that the symmetry points in the original Brillouin zone at a wave vector k become equivalent to the central symmetry point in the new reduced zone [12]. In this method, the number of atoms in the central cell (at k=0) is increased to match the real number of nanocrystal atoms. The large unit cell method is a supercell method that was suggested and first applied for the investigation of the electronic band structure of semiconductors [6-10]. This method differs from other supercell methods. Instead of adding additional k points to the reciprocal space, the number of atoms in the central cell (k=0) is increased and a larger central unit cell is formed [6]. k=0 is an essential part of the theory of LUC because it uses only one point in the reciprocal space that means only one cluster of atoms exist which is the features of quantum dots [13]. The calculations are carried out by using Gaussian 03 program [14]. The periodic boundary condition (PBC) method available in Gaussian 03 program is used to perform the present tasks [15]. The calculations were carried out for the core geometries as shown in Figs.1 and 2 .

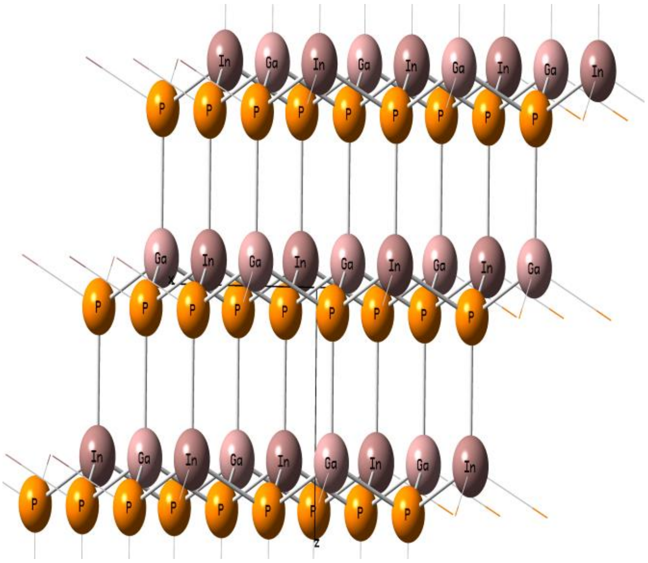

Fig. 1: (color online) $In_{0.5}Ga_{0.5}P$ 54 atoms core LUC (parallelepiped shape primitive cell multiple).

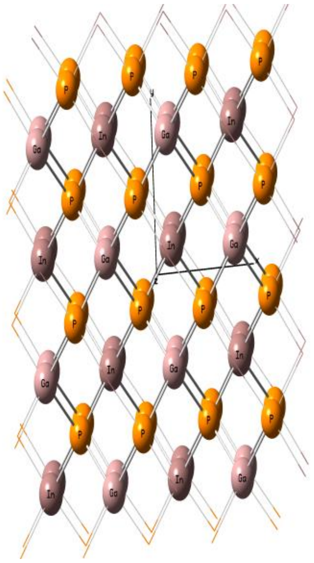

Fig. 2: (color online) $In_{0.5}Ga_{0.5}P$ 64 atoms core LUC (cubic Bravais cell multiple).

We shall use the density functional theory at the generalized gradient approximation (GGA) method level [11].

Kohn-Sham density theory [16,17] 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:

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

where $n=n_\uparrow+n_\downarrow$, and the generalized gradient approximation (GGA) [18, 19]

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

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 [20], but the best choice for $f(n_\uparrow,n_\downarrow,\nabla n_\uparrow,\nabla n_\downarrow)$ is still a matter of debate.

Results and Discussions

Figs.3 and 4 show the total energy for 54, 64 atoms respectively of $In_{0.5}Ga_{0.5}P$ nanocrystal as a function of lattice constant from which we obtained the equilibrium lattice constant. This behavior is due to the attraction forces that take place at the large distance between atoms. The stability of the nanocrystal at the equilibrium when lattice constant equal to 0.543,0.53nm respectively, while the attraction forces between the atoms equal to the repulsion [8]. Fig. 5 shows the variation of the total energy with the variation of the number of core atoms; it is shown that the total energy 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 aforementioned effects [21]. Fig.6 shows the shape effect on the energy gap, the energy gap of 8 atom core is nearer to the value of 64 atom core which is also the case between 16 atom and 54 atom. Both 8 and 64 atom core cells are cubic Bravais lattice multiple while 16 and 54 atom cores are parallelepiped primitive cell multiple. The value of $In_{0.5}Ga_{0.5}P$ energy gap is ~ 1.4eV between the energy gap of InP 1.3eV and GaP 1.63eV [5]. Although this shape effect was found in previous literature [9, 10, 15]

Fig.7 shows the valence and conduction bands with the same trend of shape effects. Bravias cubic cells (8, 64 atoms) have wider bands than primitive parallelepiped cells (16, 54) atoms. But the valence bands increases with increasing number of atoms. This effect was also recognized but with less obvious shape effects in previous studies [9, 10, 13, 15]. From Fig.8, we can notice that the value of cohesive energy decreases with increasing of the number of atoms per LUC reflecting the strong contribution of atoms. The cohesive energy increment is not linear and the rate of change of larger crystals sizes decreases. This behavior show the shape effect which appear because of shape conversion from cubic cell (8, 64) to the parallelepiped cell (16, 54) [10, 21, 22].

The property that does not show shape effects is the atomic ionicity as depicted in Fig.9. This figure shows that smaller nanocrystals are less ionic than larger ones. This property was also noticed previously in LUC calculations for other nanocrystals [15]. Density of states of core atoms LUC as a function of energy levels is shown in Figs.10 and 11. 54 core atoms states show smaller energy gap, valence and conduction band compared with 64 core atoms [15].

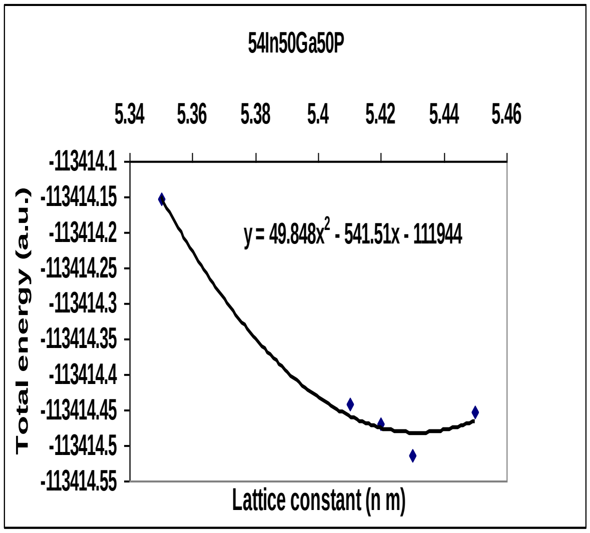

Fig.3: Total energy of 54 atoms of $In_{0.5}Ga_{0.5}P$ nanocrystal core as a function of lattice constant.

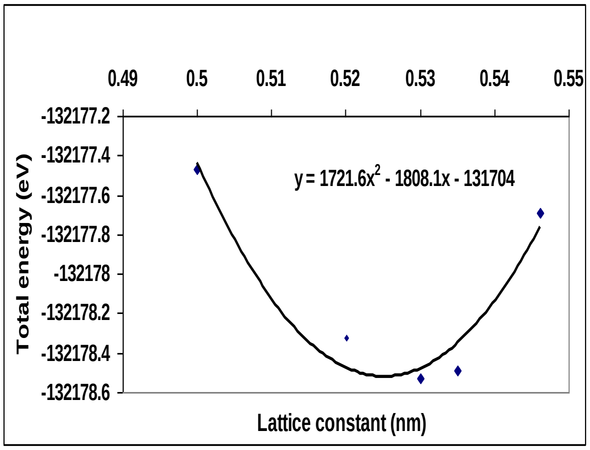

Fig.4: Total energy of 64 atoms of $In_{0.5}Ga_{0.5}P$ nanocrystal core as a function of lattice constant.

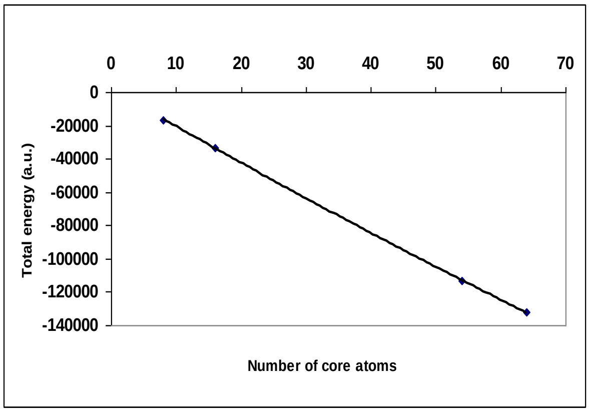

Fig.5: Total energy of the core part of $In_{0.5}Ga_{0.5}P$ nanocrystals as a function of the number of core atoms.

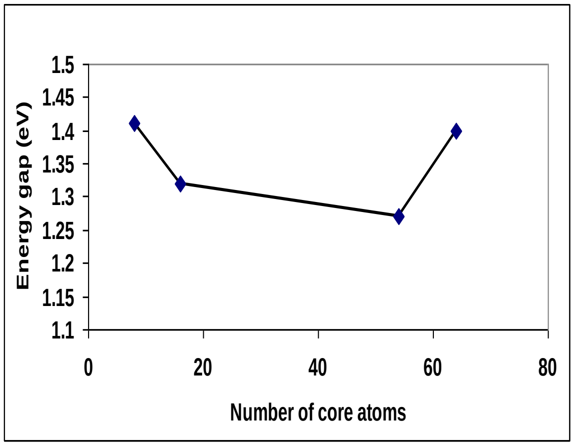

Fig.6: Energy gap of the core part of $In_{0.5}Ga_{0.5}P$ nanocrystals as a function of the number of core atoms.

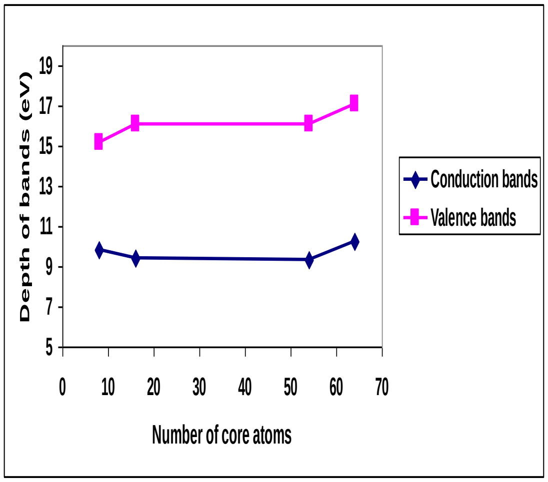

Fig.7: Valence and conduction bands variation with number of core atoms of In0.5Ga0.5P nanocrystals.

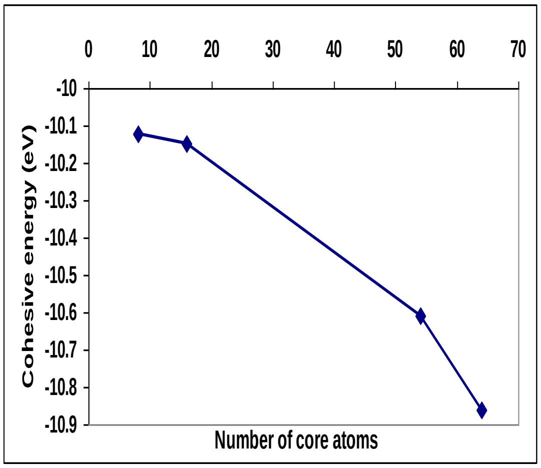

Fig.8: Cohesive energy variation with number of core atoms of $In_{0.5}Ga_{0.5}P$ nanocrystals.

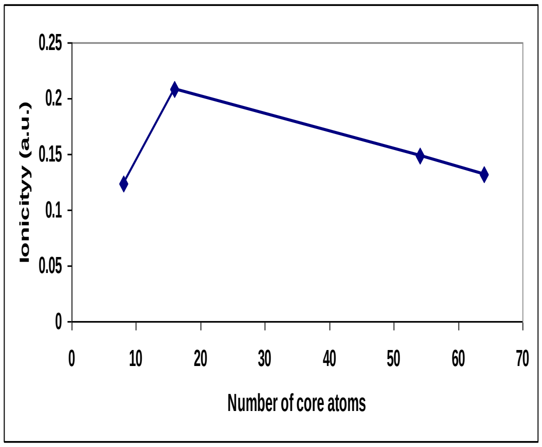

Fig.9: The Ionicity as a function of Number of core atoms for In0.5Ga0.5P nanocrystals.

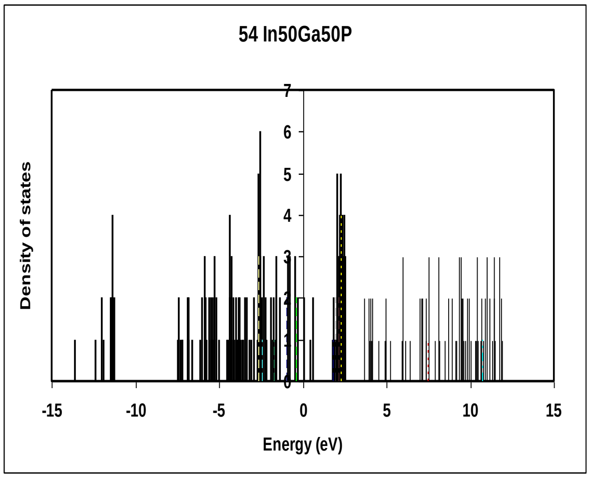

Fig.10: Density of states of 54 Core atoms of core part of $In_{0.5}Ga_{0.5}P$. Valence band are shown with bold lines while conduction band are shown with ordinary lines. The energy gap is shown between the two bands. (Eg=1.27 eV).

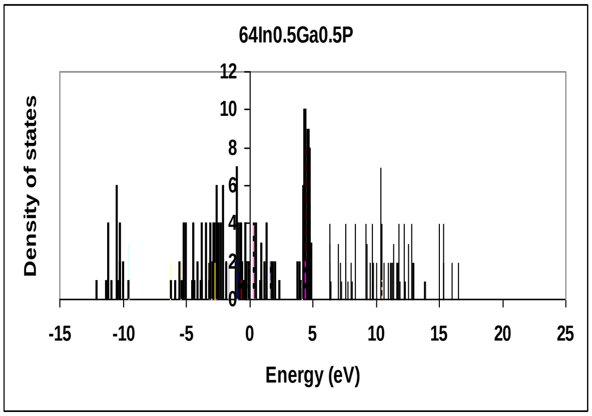

Fig.11: Density of states of 64 Core atoms of core part of $In_{0.5}Ga_{0.5}P$. Valence band are shown with bold lines while conduction band are shown with ordinary lines. The energy gap is shown between the two bands. (Eg=1.4 eV).

Conclusions

We conclude from the above results many properties of $In_{0.5}G_{0.5}aP$ nanocrystals change abruptly at the nanoscale. Calculations show that shape effects of the nanocrystal are an important factor in its electronic properties. Energy gap Total energy decrease with increasing number of core atoms, while valence band, conduction band show shape effects. However some properties such as ionicity and cohesive energy do not show this effect but decreases smoothly as nanocrystal core size increases. Degeneracy of states as a function of energy show a summary of the above mentioned shape properties.

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