Research Article

Study the Electronic Structure of In$_{1-x}$Al$_x$P with variable concentration of Aluminum using Density Functional Theory

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Abstract

The equilibrium structure and the electronic properties of III-V zinc-blende AlP, InP semiconductors and their alloy have been studied in detail from first-principles calculations. To determine properties of indium Aluminum phosphide nanocrystals as a function at size and shape density functional theory at the generalized-gradient approximation level coupled with large unit cell method is used to investigate electronic structure properties of indium aluminum phosphide nanocrystals at a function of increasing the concentration of aluminum such as the lattice constants, energy gap, valence band width, cohesive energy, density of states etc. Results show that laws that are applied at microscale alloying percentage are no more applicable at the present nanoscale. Results also show that size, shape and quantum effects are strong. Many properties fluctuate at nanoscale while others converge to definite values. Density of states summarizes many of the above quantities.

Keywords: InAlP nanocrystal , Density Functional Theory

1. Introduction

In$_{1-x}$Al$_x$P alloy provides wide bandgap energy in the non-nitride III-V semiconductors and has been wide applied in electronic and photonic devices (S. Dissanayake *et al*, 1991 ; H. X. Jiang *et al*, 1991 ; S. Krishnamurthy *et al*, 1988) . The parent (binary) compounds such as aluminum phosphide (AlP) and indium phosphide InP, are non-centrosymmetric cubic semiconductors with zinc-blende structures based on the space group F43m (M. Othman *et al*, 2009 ; R. W. G. Wyckoff , 1986). Recently, these compounds have attracted a great deal of attention, (O. Madelung and L. Bornstein , 1982 ; T. J. Coutts and S. Naseem, 1985) expecting fabrication of important electronic devices. Indeed, InP is a very promising material for solar cells and high-per- formance computing and communications (M. S. Gudiksen *et al*, 2002 ; J. F. Wang *et al*, 2001 ; D. E. C. Corbridge , 1995). Similarly, AlP, with the largest direct gap of the III-V com-pound semiconductors, is undoubtedly the most "exotic". Usually, this material is alloyed with other binary mate-rials for applications in electronic devices such as light- emitting diodes (e.g. aluminium gallium indium phosphide) (D. E. C. Corbridge , 1995). The present work will be involved in calculating electronic properties of nanocrystals as the size and shape of these nanocrystals change. We were used density
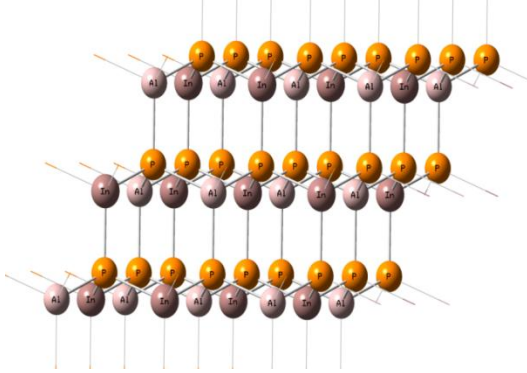
functional theory at the generalized-gradient approximation level (Perdew, Burke, and Ernzerhof PBE approximation) coupled with large unit cell method (LUC- DFT) to simulate the electronic structure of In$_{1-x}$Al$_x$P which is a well developed theory that had been applied repeatedly for the nanocrystals electronic structure .

2. Theory and calculations

Density functional theory (DFT) coupled with the large unit cell (LUC) were used in the evaluation of the electronic structure of In$_{1-x}$Al$_x$P 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 (S.M.Sze , K.K. Ng., 2007). 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 (R. Evarestov , 1975 ; A. Harker and F. Larkins, 1979; O.Ibtesam Radi *et al* , 2007 ; N. H. Aysa *et al* , 2011; M. A. Abdulsattar, 2010). 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

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larger central unit cell is formed (R. Evarestov , 1975). 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 (H.M. Abduljalil , 2011). The calculations are carried out by using Gaussian 03 program (M. J. Frisch , 2003). The periodic boundary condition (PBC) method available in Gaussian 03 program is used to perform the present tasks (M. A. Abdulsattar , 2011). The calculations were carried out for the core geometries as shown in Figs.1 and 2 .

Fig. 1: (color online) $In_{0.5}Al_{0.5}P$ 54 atoms core LUC (parallelepiped shape primitive cell multiple)
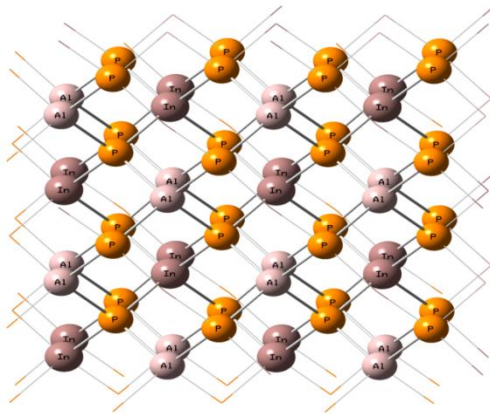
Fig. 2: (color online) $In_{0.5}Al_{0.5}P$ 64 atoms core LUC (cubic Bravais cell multiple).

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

Kohn-Sham density theory (J. Perdew et al , 1996 ; W. Kohn and I.J. Sham,1965) 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:

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

where $n = n_\uparrow + n_\downarrow$, and the generalized gradient approximation (GGA) (R. M. Dreizler and E. K. U. Gross, 1990; D. C. Langreth and M. J. Mehl, 1983) .

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

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 (J. P. Perdew,1992) but the best choice for $f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow)$ is still a matter of debate.

3. Results and discussion

Figures 3 and 4 show total energy for 54 and 64 atoms respectively of InAlP nanocrystal as a function of lattice constant, from which the equilibrium lattice constant is obtained.
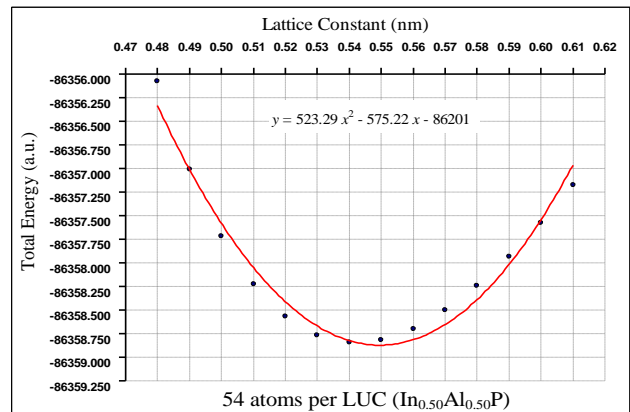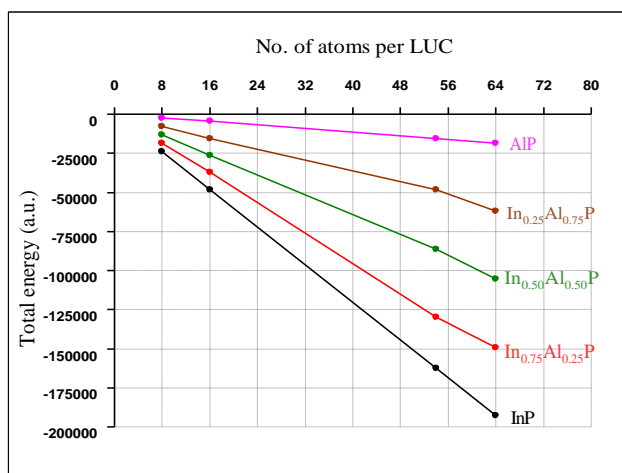

Fig. 3: Total energy of 54 atoms of $In_{0.5}Al_{0.5}P$ nanocrystal core as a function of lattice constant.
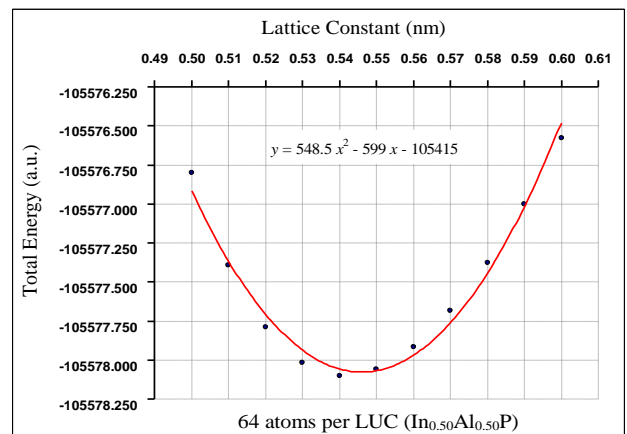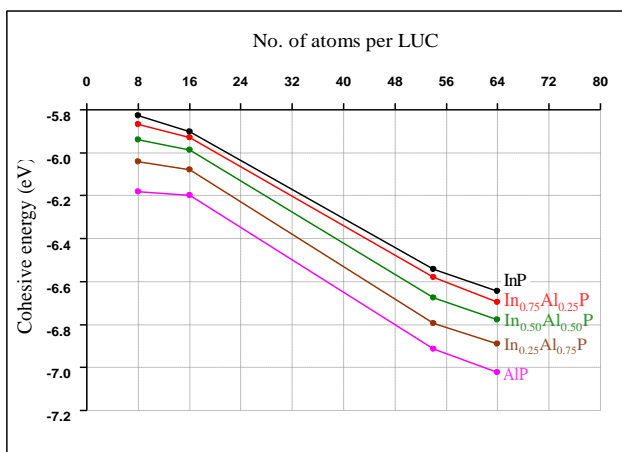

Fig. 4: Total energy of 64 atoms of $In_{0.5}Al_{0.5}P$ nanocrystal core as a function of lattice constant.

The parabolic behavior is due to attractive forces that take place at large distance between atoms and Coulomb repulsion at shorter distances. Stability of the nanocrystal is at equilibrium when lattice constant is equal to 0.54nm which the attraction and repulsion forces between atoms are equal (I. O. Radi et al, 2007).

As shown in Fig. 5, total energy of LUC increases (decreases with the negative sign) as total number of atoms and number of indium atoms increases. This is reasonable since increase in number of atoms increases the number of mutual interactions resulting in an increase in total energy. Indium atom is the heaviest atom in present ternary alloy that contains largest number of electrons. As a result total energy increases with higher fractions of indium. This effect reflects the strong contribution of kind and number of atoms.

reason is that elements of the same column tend to have greater affinity as they become lighter. This can be understood by comparing experimental and theoretical cohesive energy of group IV elements (M .A. Abdulsattar and K H Al-Bayati , 2007; M. A. Abdulsattar , 2009).

Fig. 7 shows increment of lattice constant with fraction of Aluminum. The lattice constant generally decreases with increasing number of core atoms. This behavior has been found in several previous LUC results (M .A. Abdulsattar and K H Al-Bayati , 2007; M. A. Abdulsattar , 2009) and also found experimentally for diamond.
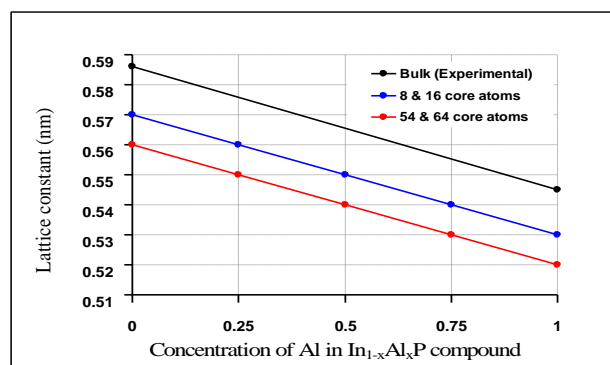
Fig. 7: Variation of lattice constant with concentration of Aluminium.

The energy gap as shown in Fig. 8 shows quantum effects. The fractions of indium x=0 (AlP), 0.5 ($In_{0.5}Al_{0.5}P$) and 1.0 (InP) are in their expected decreasing tendency. This figure shows the energy gap increases with increasing number of core atoms and increasing with concentration of Aluminum . Presently we discuss density of state Figs. Shown in 12 and 13.

Fig. 5: Total energy of the core LUC atoms of $In_{1-x}Al_xP$ nanocrystals as a function of the number of core atoms.
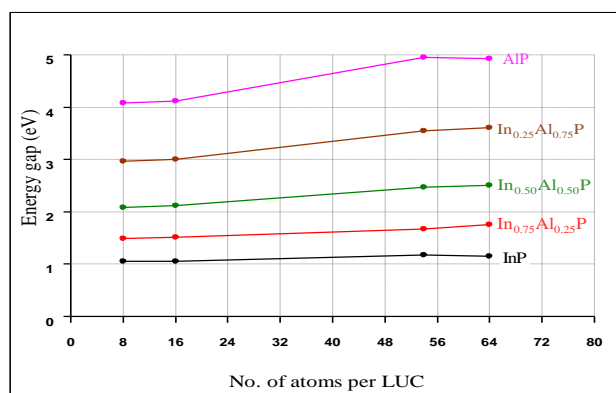

Fig. 6: Cohesive energy of the core LUC atoms of $In_{1-x}Al_xP$ nanocrystals as a function of the number of core atoms.

The cohesive energy increment shown in Fig. 6 as a function of number of atoms also holds for the same reason of total energy. However, the cohesive energy increases as a function of Al fraction instead of In,

Fig. 8: Energy gap of the core part of $In_{1-x}Al_xP$ nanocrystals as a function of the number of core atoms.

The property that usually does not show shape effects is atomic ionicity as depicted in Fig. 10. The insensitivity of this property to shape effects has been also noted previously in LUC calculations for other nanocrystals (H. M. Abduljalil , 2011). However, some fluctuations for 8 atom LUC in present work show that

small number of atoms is associated with small number of basis state expansion might have errors that change expected results for some quantities such as present atomic charges.
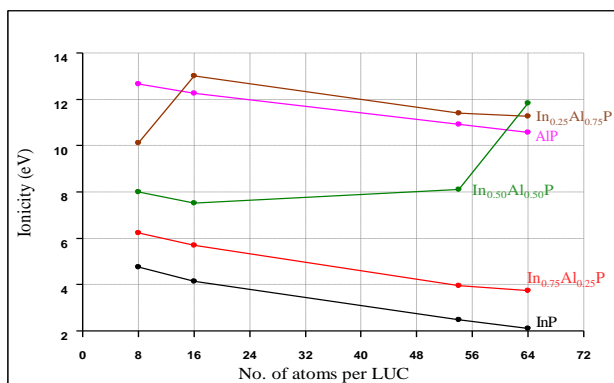

Fig. 10: The Ionicity as a function of Number of core atoms for $In_{1-x}Al_xP$ nanocrystals.

Fig. 11 shows the density of states as a function of orbital energy. The degeneracy of states has been maximum of 3 and 4 for 54 and 64 atoms respectively for considered nanocrystals. Highly degenerate states seen in the core reflects high symmetry, equal bond lengths and angles in perfect structure.
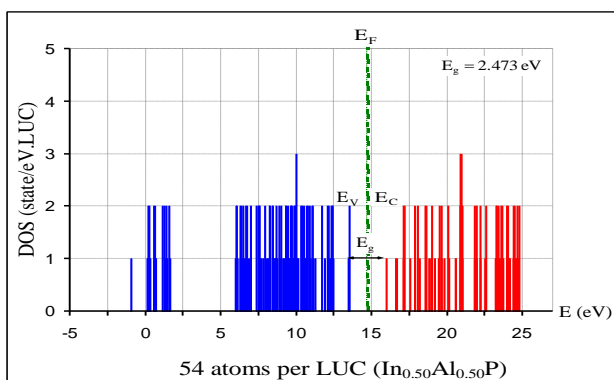

(a)
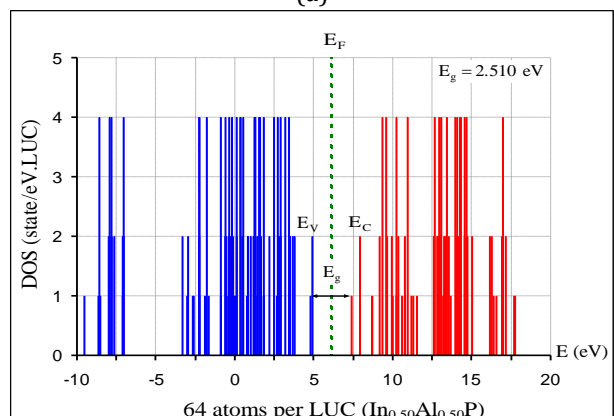
(b)

Fig. 11: Density of states of (a) 54 and (b) 64 atoms of core part of $In_{1-x}Al_xP$ nanocrystals. The energy gap is shown between the conduction and Valance bands.

Fig. 12 displays maximum density of states as a function of number of core atoms for various cells and fractions. This figure is very similar to that of the band gap. Low symmetry causes the split of equal energy (degenerate) states. This splitting causes splitted states to enter the forbidden gap and reduce energy gap. However, this is not the only factor that affects energy gap. Concentration of Al increases the gap. As a result value of energy gap interplays between symmetry and concentration of elements that compose the alloy. Lattice distortion and strain reduce high degeneracy and density of state which is another way to explain the above results.
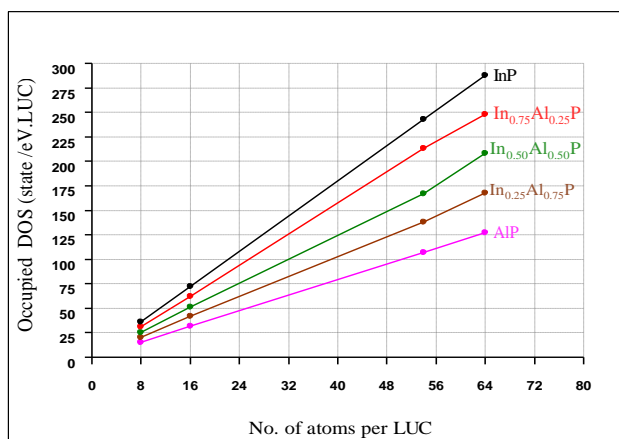
Fig. 12: Highest density of states as a function of number of core atoms in $In_{1-x}Al_xP$ nanocrystals.

Fig. 13 shows variation between indium fraction and wavelengths that corresponds to minimum gap ($\lambda = hc/Eg$). We can see that wavelength decreases with increasing the number of core atoms and increasing with concentration of Aluminum . This figure is complementary with Fig. 8 and can be explained by the same discussion basis. In addition to present investigation of InAlP nanocrystals, investigation also includes InP and AlP nanocrystals and can be extended to bulk properties (A. R. Degheidy *et al* , 2012) .
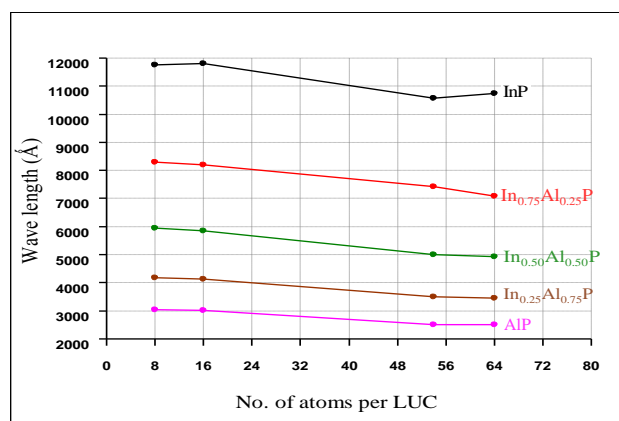
Fig. 13: Variation of threshold absorption wavelength that corresponds to the minimum energy gap as a function of the Aluminum fraction.

Conclusions

Calculations show that shape, size, symmetry and elements alloying percentage are important factors of its electronic properties. All properties are affected by the size and alloying percentage such as total energy, cohesive energy and ionicity. Energy gap is affected by above factors in addition to quantum symmetry and density of states. Density of states shows highest degeneracy of states and wavelength for indium concentration (x=1), which correspond to InP and AlP respectively.

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