

Comparison GaP nanocrystal pure and doped with three atoms of Indium: Density functional theory study

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ABSTRACT

Ab initio restricted Hartree-Fock method coupled with the density functional theory method is used to determine the electronic structure and physical properties of pure Gallium phosphide (GaP) nanocrystal and mixed Gallium phosphide (GaP) nanocrystal with three atoms Indium (In) have been studied within the framework of Density functional theory using diamondoid structure, begin Diamantane, Tetramantane, Hexamantane and Octamantane, depended on simulation electronic structure of GaP nanocrystal. In order to full investigate the substitution of Ga by in on structural, gap energy, charge distribution, density of states, tetrahedral angle, dihedral angle, bond length. The results of electronic structure calculations are compared to the same size gallium and phosphide nanocrystals. The comparison reveals that the energy gap of the two kinds of nanocrystals. With remarkable dependence on the shape of the molecule or nanocrystal. The result show the energy gap decreases as a function of the total number of Ga and P atoms in most of the investigated range. Three atoms of Indium (In) to diamantoids GaP the effect of Indium shows a clear convergence in HOMO and LUMO levels. And effect of Indium shows in increased energy gap of GaInP diamantine.

KEY WORDS: Diamondoids, Gallium phosphide (GaP), nanocrystal, density functional theory (DFT).

1. INTRODUCTION

During last year's many efforts have been carried out to increase the efficiency in Diamondoids due to their role in nanotechnology. Diamondoids has several the cages nature of like as Adamantane Diamantane, Tetramantane, Hexamantane and Octamantane. One of the most-important properties of a semiconductor is that it can be doped different types and concentrations of impurities to vary its resistivity. Also, when these impurities are ionized and the carriers are depleted, they leave behind a charge density that result in an electric field and sometimes a potential barrier inside the semiconductor. Such properties are absent in a metal or an insulator. Gallium phosphide is a semiconductor with an indirect band gap in its zincblende structure. This semiconductor has allotropic zincblende (cubic) and wurtzite (hexagonal) phases. Its gap in the visible light range, at 2.26 eV, makes it a natural candidate for use in light emitting diodes (LEDs). We shall investigate compared of GaP nanocrystals pure and doped with substitution three atoms of Indium (In). Indium gallium phosphide (InGaP), also called gallium indium phosphide (GaInP), 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. Some semiconductor devices such as EFluor Nanocrystal utilise In GaP as their core particle. Indium gallium phosphide is a solid solution of indium phosphide and phosphide. Ternary alloy is an attractive material for preparation of variety of optoelectronic and microelectronic devices. The band gap energy is usually determined using a parabolic interpolation between GaP and InP. (Figs.(1-2)) show The investigation of size-variable GaP diamondoids to reach the properties of GaP nanocrystals pure and doped with substitution three atoms of Indium (In) and bulk limits will be the subject of the present work.



Figure.1. Colour online) Geometrically optimized GaP- tetramantane and GaInP-tetramantane

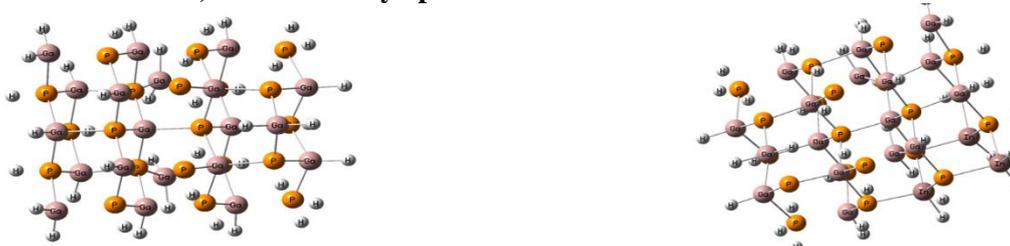


Figure.2. Colour online) Geometrically optimized GaP- octamantane and Ga InP-octamantane

2. METHODS & MATERIALS

Theory: The geometrical optimization calculations are performed with simultaneous optimization and complete convergence of maximum displacements. The final geometrically optimized nanocrystal using density functional theory (DFT). Density-functional theory is widely accepted as a framework for the study of the electronic ground-state properties of molecules and solids. It has long been realized that the molecular bond energies and the cohesive energies of the solids are overestimated when the electronic exchange and correlation effects. However, the development of nonlocal exchange and correlation functional has demonstrated that the bond energies of molecules, the cohesive energies of solids, and the energy barriers for molecular reactions can be greatly improved within density-functional theory. We use the DFT at the generalized gradient. Diamond or zinc blende structured materials. The calculations are carried out using Gaussian 09 program Perdew Burke Emzerhof (PBE) using (3-21Gd) basis states. The Gaussian 09 program used in the present work. Solid-state programs are more recent and require higher computational resources to include the physical and chemical properties previously included in molecular approaches. The nano-scale region, which is the intermediate region between the molecular and bulk limits, can be approached from one of two approaches, namely, the bottom-up or top-down methods taken from molecular and solid-state theories respectively. These molecules include GaP-diamantane, ($\text{Ga}_7\text{P}_7\text{H}_{20}$), GaP-tetramantane ($\text{Ga}_{11}\text{P}_{11}\text{H}_{28}$), GaP-hexamantane ($\text{Ga}_{13}\text{P}_{13}\text{H}_{30}$) and GaP-octamantane ($\text{Ga}_{20}\text{P}_{20}\text{H}_{42}$). The number of cages of these diamondoids is obvious from the nomenclature of the latter four. The largest considered GaP diamondoid is GaP-octamantane. When add three atoms Indium is becomes include GaInP diamantine ($\text{Ga}_4\text{In}_3\text{P}_7\text{H}_{20}$), GaP-tetramantane ($\text{Ga}_8\text{In}_3\text{P}_{11}\text{H}_{28}$), GaP-hexamantane ($\text{Ga}_{10}\text{In}_3\text{P}_{13}\text{H}_{30}$) and GaP-octamantane ($\text{Ga}_{17}\text{In}_3\text{P}_{20}\text{H}_{42}$).

3. RESULTS AND DISCUSSION

In Fig. (3-a) Note that the total energy increasingly negative direction as a function for number of atoms and this shows stable (GaP) diamondoids and fig.(3-b), remain stable (GaInP) diamondoids in spite of the addition of three atoms of indium. This stable back to the unique physicochemical properties of diamondoids due to their exceptional atomic. Fig.(4-a), Shows the distribution of bond lengths in GaP-diamondoids. The dashed line represents the experimental value of GaP bulk bond length at 2.36 Å. The figure starts with a sharp, high value for the number of (P-H) phosphorus-hydrogen bonds. The phosphorus-hydrogen bonds are the shortest bonds in the present molecules. Fig. (4-b) Shows the distribution of bond lengths in GaInP-diamondoids. In this figure can be seen the phosphorus-hydrogen bonds are the shortest bonds (1.44 Å) and phosphorus Indium bond are the longest bonds (2.58 Å). Fig. (5-a) it can be seen that the energy gap decreases as a function of the total number of Ga and P atoms in most of the investigated range. The exceptions are between GaP-tetramantane and GaP-hexamantane. The reason for this deviation is the effect of the shape of the GaP diamondoids same effect for GaInP diamondoids. Also in Figure (5-a) both HOMO and LUMO energy levels are negative. This shows that neither adding nor removing electrons from GaP diamondoids are energetically favorable. This reflects the high stability and inertness of the present diamondoids structure. In fig (5-b) the energy gap decreases as a function of the total number of Ga, in and P atoms in most of the investigated range. The exceptions are between GaInP-tetramantane and GaInP-hexamantane. The reason for this deviation is the effect of the shape of the GaInP diamondoids. Also in Figure.(5-b) both HOMO and LUMO energy levels are negative. But level HOMO is very near level LUMO.

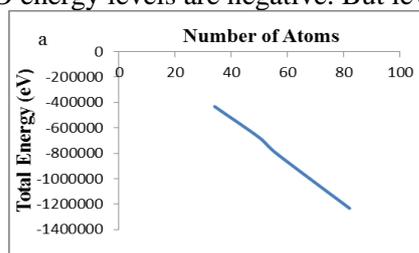


Figure.(3-a). Total as a function for number of atoms (GaP) diamondoids

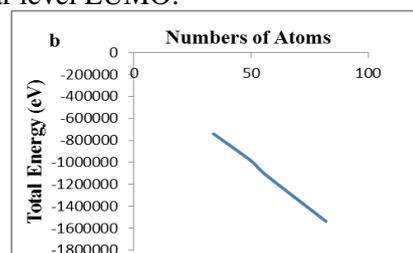


Figure.(3-b). Total as a function for number of atoms (Ga InP) diamondoids

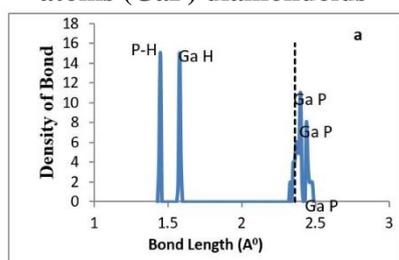


Figure. (4-a). Shows the distribution of bond lengths in GaP-diamondoids

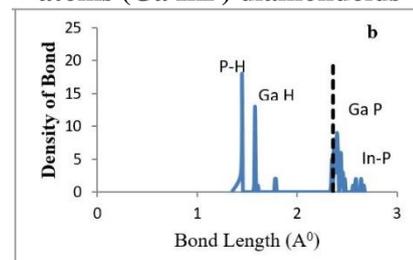


Figure. (4-b). Shows the distribution of bond lengths in Ga InP-diamondoids

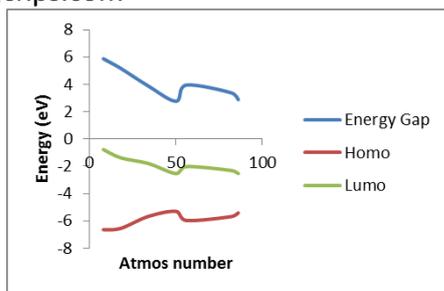


Figure.(5-a). Energy gap as a function for number of atoms (GaP) diamondoids and both HOMO and LUMO energy levels

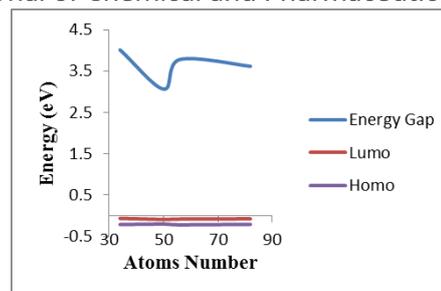


Figure.(5-b). Energy gap as a function for number of atoms (Ga InP) diamondoids and both HOMO and LUMO energy levels

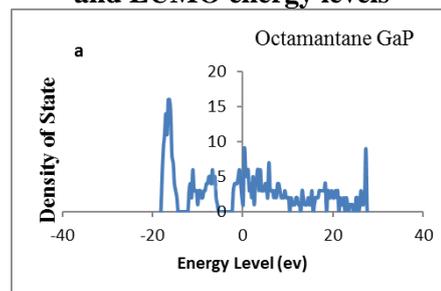
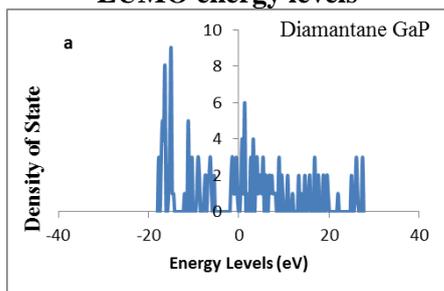


Figure.(6-a). Density of energy states of geometrically optimized GaP-diamantane and (GaP-octamantane), as a function of energy level. The dotted line represents the Fermi level

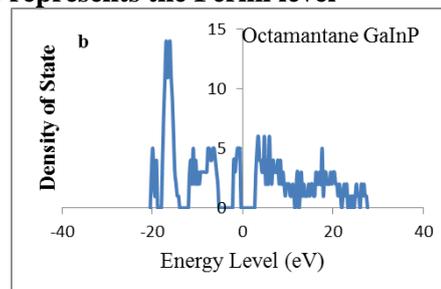
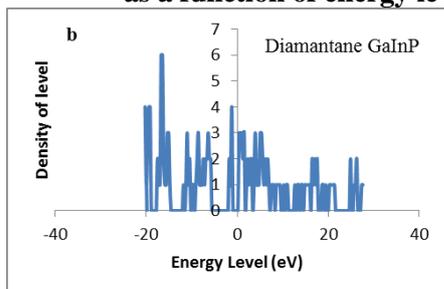


Figure.(6-b). Density of energy states of geometrically optimized GaInP-diamantane and GaInP-octamantane, as a function of energy level. The dotted line represents the Fermi level

Figure.(6-a) shows the density of energy states of geometrically optimized GaP-diamantane and GaP-octamantane as a function of energy level. The values of the energy gap (3.83 and 3.6 eV respectively) the bulk value (2.26 eV) as expected in this range. The near-discrete levels of diamantane turn into the near-continuous band structure of decaoctamantane, which is nearer to the bulk. Fig.(6-b), shows the density of energy states of geometrically optimized GaInP-diamantane and GaInP-octamantane as a function of energy level. The values of the energy gap (4.0 and 3.6 eV respectively).

Fig.(7-a) shows the distribution of the values of GaP tetramantane and GaP- hexamantane tetrahedral angles. The ideal bulk zinblende value of this angle at 109.47° is shown. The highest peak shifted one or two degrees from this value in tetramantane GaP either in the hexamantane GaP experimental value Located in the center of the highest peak. Fig.(7-b), shows the distribution of the values of GaInP tetramantane and GaInP- hexamantane tetrahedral angles. The highest peak shifted one or two degrees from this value in tetramantane GaInP either in the hexamantane GaInP experimental value applies to the highest peak then approaching the bulk. Where the dash line represents the experimental value. Surface relaxation is responsible for this distribution, as it leads to the deviation of these angles from their ideal value.

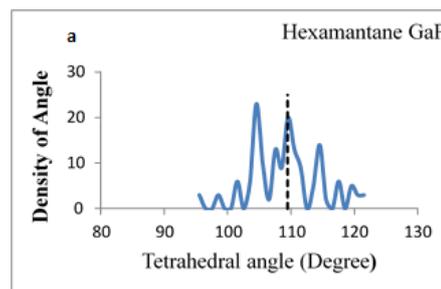
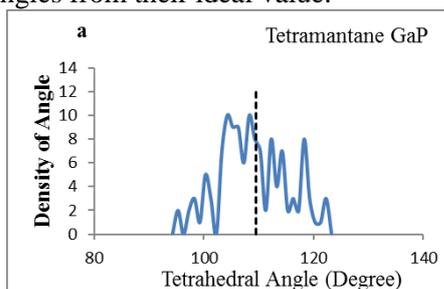


Figure.(7-a). Distribution of the values of GaP-tetramantane and GaP- hexamantane tetrahedral angles

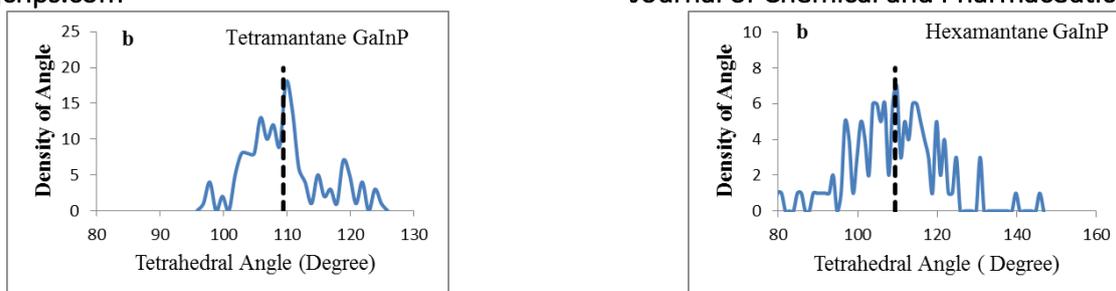


Figure.(7-b). Distribution of the values of GaInP-tetramantane and GaInP-hexamantane tetrahedral angles..The dashed line represents the ideal bulk zincblende value of this angle, at 109.47°.

Fig.(8-a) it can be seen the dihedral angle. The ideal bulk zincblende values of these angles are ± 60 and ± 180 . Again, surface relaxation is responsible for the narrow deviation from these ideal values. The GaP-diamantane angles are more distant from the ideal value than in the case of GaP-octamantane. Surface relaxation is responsible for this distribution, as it leads to the deviation of these angles from their ideal value. As well as diamantine GaInP is far from the ideal value. But the highest peak shifted one or two degrees from this value in octamantane. Fig.(9-a), shows Milliken atomic charges of octamantane GaP surface as a function of layers depth using the slab geometry method. The first and last negative charged atoms in the Figure are hydrogen atoms. The second atoms are neighboring the outermost surface phosphide atoms that have negative charges. The third layer hydrogen neighbor layer to gallium atoms has positively charges. The fourth layer has nearly zero charge from which core layers begin. This trend of charges is consistent with our previous assumptions of thickness of surface reconstruction effects. Fig. (9-b) Shows Milliken atomic charges of octamantane GaInP surface as a function of layers depth. The first and last negative charged atoms in the Figure are hydrogen atoms. The second atoms are neighboring the outermost surface phosphide atoms that have negative charges. The third layer hydrogen neighbor layer to gallium and Indium atoms has positively charges. The fourth layer has nearly zero charge from which core layers begin.

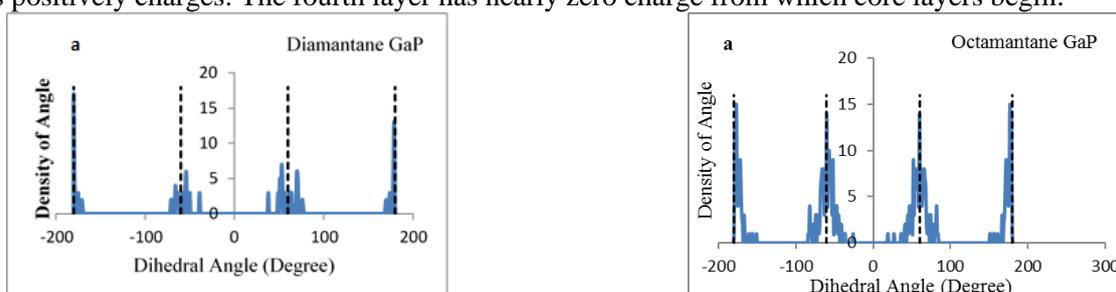


Figure.(8-a). Distribution of GaP-diamantane and GaP-octamantane dihedral angles

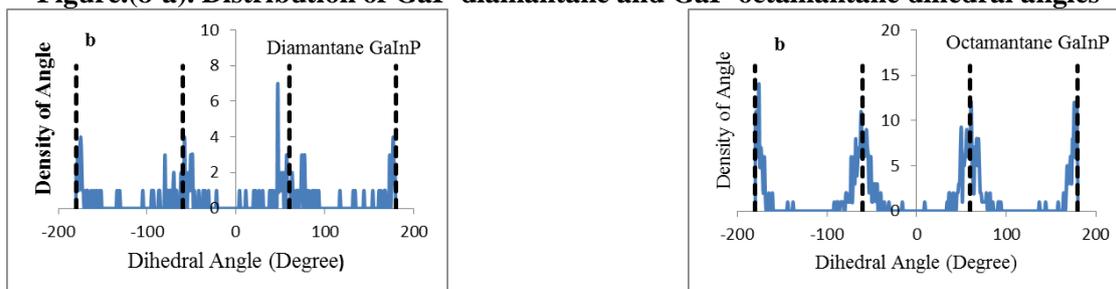


Figure.(8-b). Distribution of GaInP-diamantane and GaInP-octamantane dihedral angles. The dashed lines represent the ideal values of zincblende structure at -180° , -60° , 60° and 180°

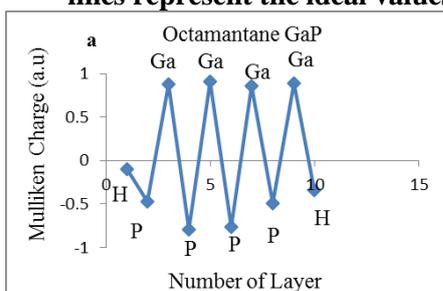


Figure.(9-a). Atomic charges as a function of layers depth of GaP octamantane nanocrystal surface stoichiometry using slab geometry.

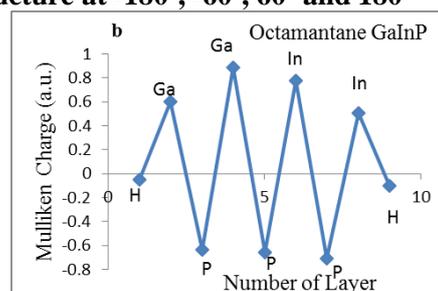


Figure.(9-b). Atomic charges as a function of layers depth of GaInP octamantane nanocrystal surface stoichiometry using slab geometry.

4. CONCLUSIONS

GaP diamondoids make their electronic structural and vibrational properties as close as possible to those of bulk zincblende structure. Which are molecular/nano-particles with minimal surface effects. Diamondoids show minimal surface relaxation effects, which can be deduced from their tetrahedral angles and dihedral angles. The main reason for the nonequivalent bond lengths in our case is the location of atoms either near or far from the surface, the shortest bond length P-H and longest bond length InP. Added three atoms of Indium (In) to diamondoids, although the indium metal component of the Period 5. Period 5 contains the heaviest few elements that have biological roles. The effect of Indium shows a clear convergence in HOMO and LUMO levels in GaInP diamondoids. The effect of Indium shows in increased energy gap of GaInP Diamondine. The energy gap decreases as a function of the total number of Ga and P atoms in most of the investigated range. The exceptions are between GaP-tetramantane and GaP-hexamantane. The reason for this deviation is the effect of the shape of the GaP diamondoids same effect of GaInP diamondoids.

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