PHASE TRANSITION OF GALLIUM ARSENIDEWURTZITE MOLECULES AND NANOCRYSTALS: A DFT STUDY

H. A. FAYYADH[a], T. H. MAHMOOD[b], E. K. HASAN[c]
[a]Open Education College, Ministry of Education, Baghdad, Iraq
[b]Department of Physics, College of Science for Women, University of Baghdad, Baghdad, Iraq
[c]Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

This paper presents a detailed analysis of electronicstructure andspectroscopiccharacteristics of GaAsmolecules andWurtzoid nanostructure using density functional theory methods. The results show that the energy gap of GaAs isfluctuated about to the experimental bulk energy gap (1.42 eV).Results of spectroscopic propertiesincluding IR and Raman spectrum, reduced mass and force constantare in good agreement with available experimental results.Study of the Gibbs free energy proved the stability phase of GaAs wurtzoids against transition to GaAs diamondoids structure.

1. Introduction

III–V semiconducting materials like Gallium arsenide (GaAs) in each of nanoandbulk forms were always taken under consideration as valuable materials from fundamental and technological [1, 2] viewpoints as a result of their massivepotentials for various optoelectronic implementation and due to their possible ability for replacing silicon in micro-electronic components as well,requiring high carrier mobility [3]. Those applications have been based on manypreferable characteristics like the vibrational, thermal conductivity, direct band gap, andhigh electron mobility.A wide range ofparameters for band structure of GaAs are famous for a greater accuracy in comparison to any of the other compound semiconductors. Which is particularlyaccurate of the basic gap ofenergy with a value of 1.42eV [4, 5]. In general, those materials have a usual cubic zinc blende (ZB) crystal structure at the ambient conditions in the bulk form [6]. However, recently it has been shown that these compounds can also be grown in other crystal phases which are not possible in the bulk form like the wurtzite (WZ).The wurtzite phasediscoverybesides the cubic zinc blende phase presents the new way to innovative physics and nano-structure applicationideasbecause of the electronic structure variation with crystal structure [7, 8].

The purpose of this work investigates the electronic characteristics of GaAs molecules,wurtzoids nano-crystalsand spectroscopic propertiesas well as the stability phase transition using density functional theory method.

2. Theory

Binary compounds in periodic table are typically existent in severalcommon phases, including ZB, rock-salt, and WZ structures. Those phases are oneswhich are projected to undergo growth for the GaAs nano-crystals. Typically, GaAs are available in zinc-blende phase at usual conditions. None-the-less, the compoundscan be found in the WZ phase in the case where they are grown on a number ofsubstratekinds [9, 10].Wurtzoids can be defined as molecules carrying the characteristics of bulk WZ phase in molecular-nanoscale size. Those molecules are of orientations of preferred axis which are alike (c axis in the WZ phase) and other 2similar axes (a and b). Those

wurtzoids are created from capped and bundled (3, 0) nano-tubes [11].The simplest atoms can be represented as in Fig1(c).by elongating this molecule in the c axis, it is possible to obtain the 2nd WZ molecule referred to as the bare wurtzoid-2c as in Fig1 (d)for GaAs wurtzoid-2c.The GaAs wurtzoid-2c stoichiometry is ($Ga_{13}As_{13}$). Bundling 3 GaAs wurtzoids parallel in thecaxescreatesGaAs tri-wurtzoid ($Ga_{21}As_{21}$) as in Fig1 (e) for bare case [11].Density functional theory (DFT) at B3LYP level ("Becke, threeparameter, Lee-Yang-Parr") has beenutilized, combined with 6-311G**basis sets [12, 14] in this research. All computation arecarriedoutwith the use of Gauss09software [13, 15, 16].
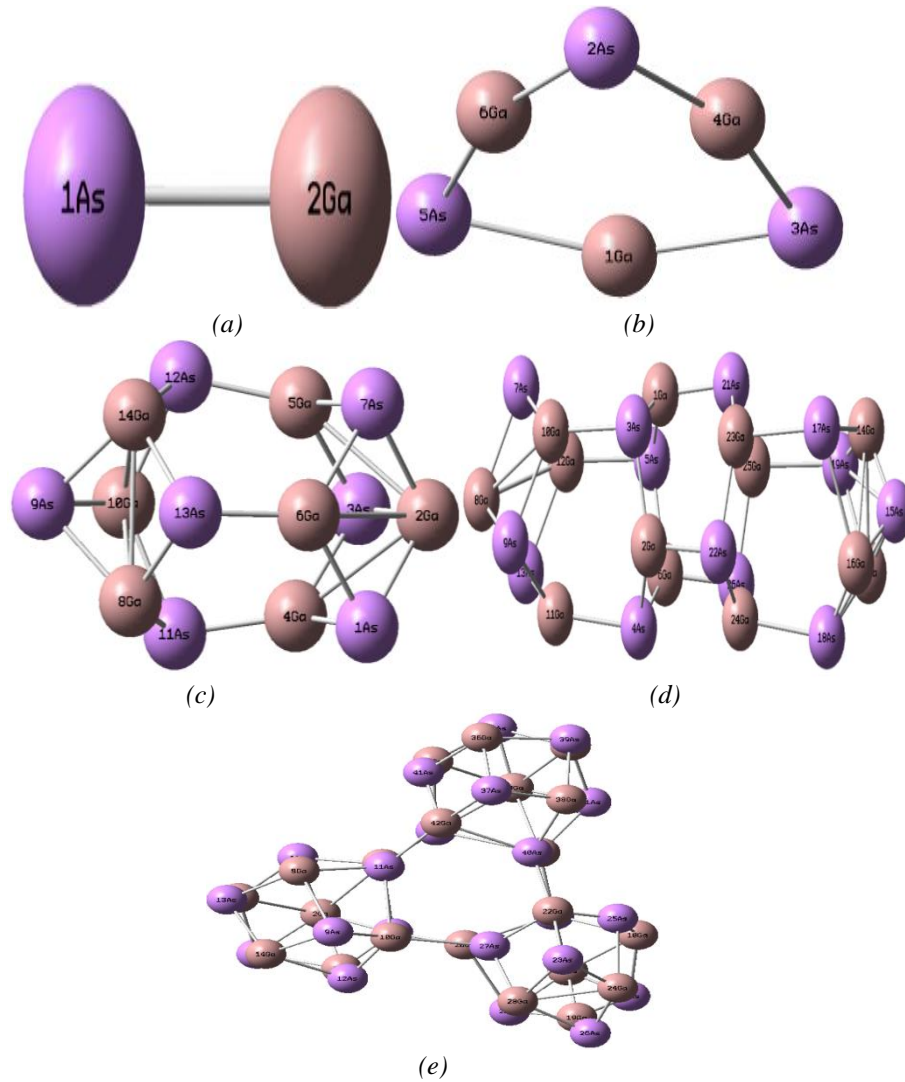

(a)   *(b)*

(c)   *(d)*

(e)

Fig. 1. GaAs Wurtzoid Nanotube Geometrical Optimization Structure: (a) GaAsmolecule;
(b) Ga₃As₃Cyclohexane; (c) Ga₇As₇wurtzoid; (d) Ga₁₃As₁₃wurtzoid2c and (e) Ga₂₁As₂₁triwurtzoid.

3. Results and discussions

The energy gap of cases under consideration, which include wurtzoids are shown in Figure (2) also compared to bulk experimental value (1.42 eV) of GaAs wurtzite phase[4,5].The moleculesenergy gaps are less compared to theenergy gaps of the bulk. The maximum energy gap of the wurtzoids is for the tri-wurtzoidsofGaAs, whichare equal to 1.71eV (the entire number of Ga and As atoms=42), this molecule is almost of a spherical shape with minimal number of the surface dangling bonds explaining its high gap ofenergy. The elongation of this molecule in c orientation for producingwurtzoid-2c decreases the gap value due to the increased number of the

surface dangling bonds. Continuously elongating those structures in their nano-tubesdirection (i.e. the directionof the c parameter) creates GaAs nanowires.
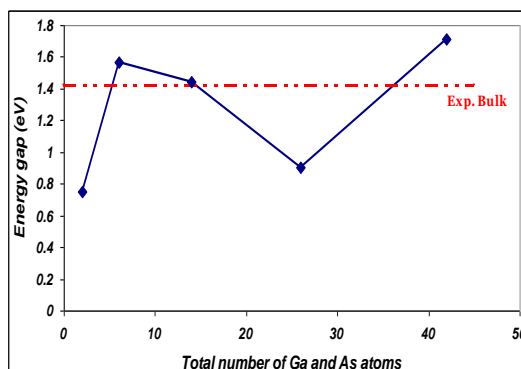

Fig. 2. Energy gap of GaAs wurtziodin compare with Bulk Experimental Energy Gap= 1.42eV [4, 5].

Fig. 3 illustrates the bond lengths distribution of the GaAs wurtzoid. There are 3bond typesin those species, which are Ga-Ga, As-As, andGa-As. The minimal bonds are Ga-As followed by the As-As. The widest bond lengthdistribution is in the (Ga - Ga) bonds.
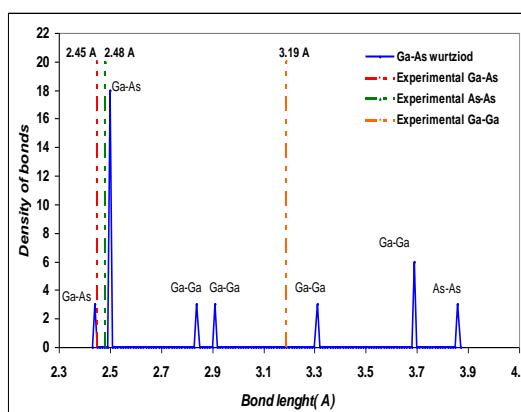

Fig. 3. Density of bond length of Ga_7As_7 (wurtziod) compare with experimental Ga-As,
Ga – Ga, As - As bond lengths are illustrated [14, 15, 17, 18].

Fig. 4 indicates that density of states of wurtziod(Ga_7As_7) as functions of energy levels. It is found that the band gap (between HOMO (V.B) and LUMO(C.B)) of wurtzoid with exist H-atoms passivated increasing about the experimental value of molecule GaAs of (4.81 eV), while the bare of this structure is 1.44 eV closed to experimental value of GaAs wurtzite (1.42eV)[4], that means the wurtzoid structure with H-passivated(HP) near to nano-scale lead to increases value of energy gap. Also, the density of statesof wurtzoid with exist H-atoms passivated have degenerated of states are lower than of the bare of this structure.
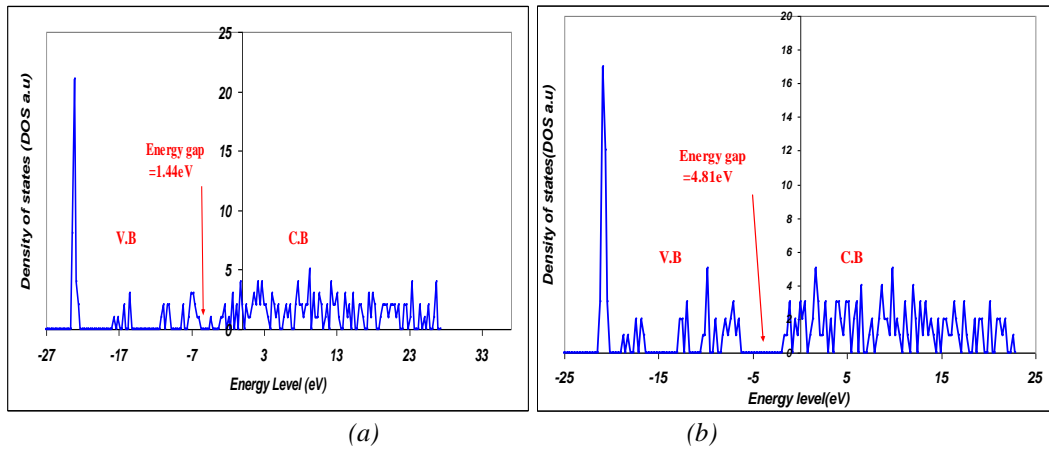
Fig. 4. (a) Density of state (DOS) of Ga_7As_7 bare wurtzoid as a function of energy levels;
(b) Density of state of $Ga_7As_7H_{14}$ HP wurtzoid as a function of energy levels.

Fig. 5 shows the maximal reduced mass mode which is utilized for nano-crystalsandmolecules for the determination of longitudinaloptical(LO) mode at bulk structure for Ga_7As_7 wurtziod. In this figureappear highest reduced mass mode (HRMM) is equal282cm^{-1} for Ga_7As_7 (wurtziod) compare with bulk experimental LO mode (285.2 cm^{-1})[20,21].
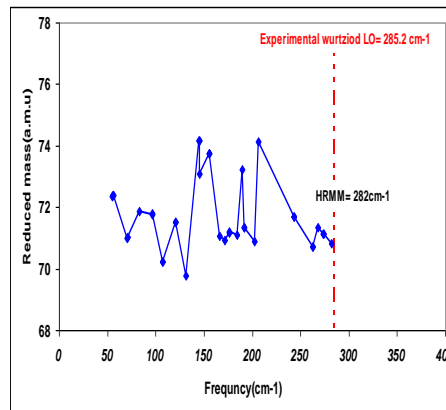

Fig. 5. Reduced mass as a frequency function of Ga_7As_7 wurtziod.

Fig. 6. shows the vibration ofGa_7As_7 wurtziodvibrational force constant as a frequency function which appear of parable shape according to relation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu'}}$$

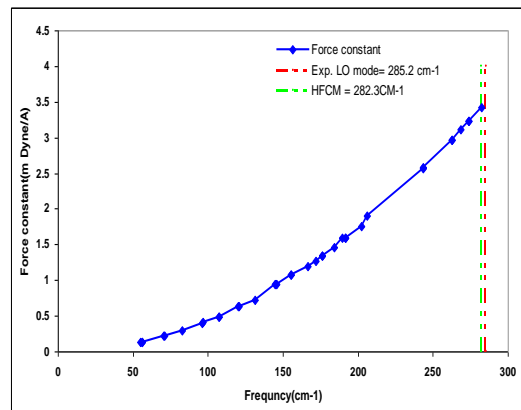where k stands for the force constant, and μ'represents the reduced mass.

Fig. 6. Force constant as a function of frequency of Ga$_7$As$_7$wurtziod.

Fig. 7 (a) shows IR intensity spectrum, which is observed two regions for Ga$_7$As$_7$wurtziod the first (155-185) cm^{-1} where the center peak at 175.9cm^{-1} and the second region center at 341.5 cm^{-1} .While fig. (7-b) is reveal Raman spectrum which are very low intensity in these two bands.WhereasBulk GaAs is identified by its infra-red absorption at about 0-300cm^{-1} vibrational mode peak[22,23].
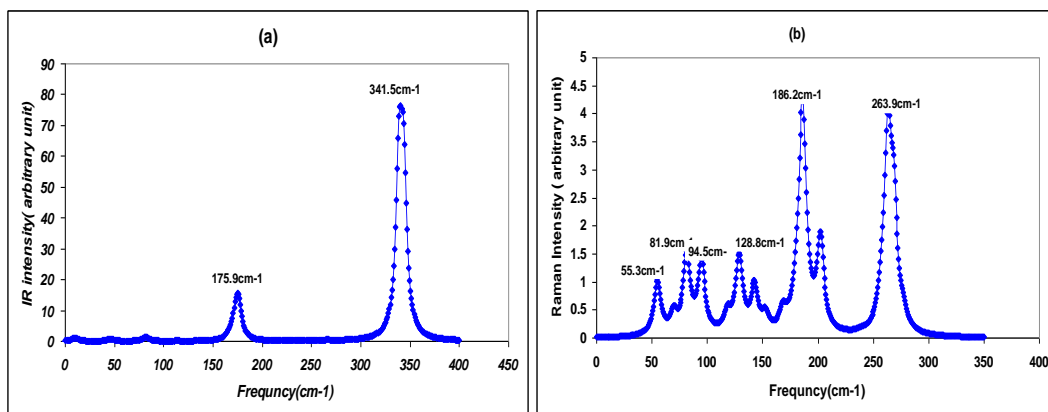

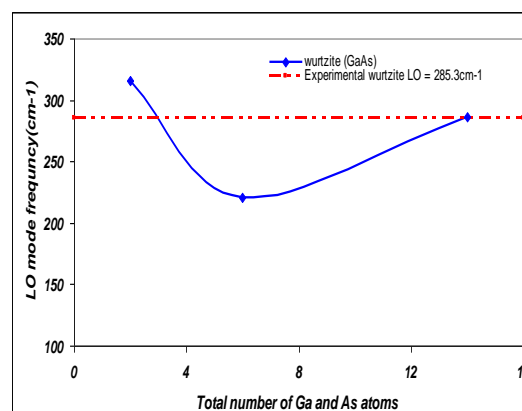*Fig. 7. (a)IR and (b) Raman intensityspectrumas a function of frequency of Ga$_7$As$_7$ wurtziod.*

Fig. 8. LO vibrational mode of GaAs wurtziod as a Ga and As atoms' function.

Fig. 8 depicts theLO vibrational mode of GaAs wurtziod as a Ga and As atoms function which decrease the value of LO mode frequency with increasing the number of atoms of GaAs wurtziod.In contrast to the case of theenergy gap, the impact of thenano-scale is reducing LO mode frequencyvalue [20,24].

It can be observed that the GaAs wurtziod with (HP) more stable than the GaAsdiamantane (HP) due to the Gibbs free energy(Gf) has high(negative) for as mention in Table (1) after take absolute value of them. The diamantane has number of bonds than wurtzoid therefore the dangling bonds be more on their surface, than the passivation of H –atom be large, this effect on values of the energy gaps.

Table 1. The relation among several parameters associated GaAs wurtziod (bare and H-passivated) with GaAsdiamantane.

Structure	Formula	Energy Gap (E_g)eV	Gibbs Free Energy Gf (eV)	Dangling bonds
Wurtzoid GaAs(Bare)	Ga_7As_7	1.44	-11.64	14
Diamantane GaAs(Bare)	Ga_7As_7	1.98	-11.68	20
Wurtzoid GaAs (Hp)	$Ga_7As_7H_{14}$	4.81	-12.26	0
Partial Diamantane(HP)	$Ga_7As_7 H_{14}$	1.42	-11.97	6

Gibbs Free Energy(Gf) computes as results of subtracting the energy number of clusters from the bulk material. The negative value of (Gf) is spontaneous processes can represent a maximum of work possible [25,26] The absolute values of negative(Gf) give high values of wurtzoid and low of diamantane. This belongs to dangling bonds at the fifth column as in Table (1). As a result of these reasons will transform to wurtzoid from diamantane at a constant of the pressure and temperature, in all the cases the wurtzoid be will more stable with Hp.

The value of energy gap for Diamantane ($Ga_7As_7H_{14}$) is lower than that of wurtzoid($Ga_7As_7 H_{14}$) for (H-passivated) case as shown in the table 1, because of the dangling bonds of them.

4. Conclusions

In this work the electronic characteristics of the GaAs wurtzoids approach to bulk limitsand nano-crystals. Structural parameters likethe lengths of thebondshadavaluedistributionwhere the highest peaks are closer to the optimal values ofbulk of those parameters. Results show the energy gap was fluctuated around the experimental bulk gap which generally confined upper wurtzoids. Results of vibrational frequencies such as reduced mass and force constantare very converge to their ideal bulk value. In addition to this we have found that the Longitudinal optical (LO) vibrational modedecrease with the increase in the number of GaAs wurtziod atoms and near to ideal bulk value, as well as IR, Raman spectrum intensity are agreement with respect to experimental bulk.The calculations of the Gibbs free energy found that the transformation to the wurtzoid phase(HP) were most stable than diamantane structure .

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