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Research paper

A study on structural and electronic properties of $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ alloys

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Abstract

We have performed first principles method to investigate structural and electronic properties of $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ ternary semiconductor alloy using Density Functional Theory and pseudo potential method within the Generalized Gradient Approximations and Local Density Approximation. The Zinc-Blende phase is found stable for GaAsN and GaAsBi alloys. In this study we investigate the both bowing parameters changing with Bismuth concentration in GaAsBi and Nitrogen concentration in GaAsN alloys. By using the bowing parameter of GaAsBi and GaAsN alloys we obtained the bandgap energies for all x concentrations ($0 < x < 1$) and lattice constant of both alloys which are important for wide range device application. For studied materials, lattice parameters and band gap energies are compared with available theoretical and experimental works.

Keywords: *III-V Semiconductors; Density Functional Theory; Electronic Properties; Structural Properties.*

1. Introduction

It is well known fact that, III-V semiconductor alloys are widely used in electronic and optoelectronic device technology. Nitrogen (N) and Bismuth (Bi) inclusive III-V semiconductor alloys provide opportunities to engineer material properties and they are also suitable for a variety of electronic and optoelectronic device applications. In recent years, the semiconductor alloys $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ have great attention as promising materials for long wavelength optoelectronic device applications. These alloys have strong band gap tunability [1], [2] and exhibit a much greater reduction of the bandgap energy with increasing x than predicted by the linear trend of the virtual crystal approximation (VCA). The bismuth alloy $GaAs_{1-x}Bi_x$ is complementary to nitrides because incorporating Bi in GaAs perturbs the valence band, whereas N in GaAs perturbs the conduction band. Both alloys show a giant band gap bowing effect in which a small amount of element Bi or N causes a large reduction in the band gap [3-5].
In this study we have investigated the electronic and structural properties of GaAsN and GaAsBi ternary alloys with the help of the density function theory. We compare the band gap reduction in both ternary alloys with increasing the guest atoms in the host lattice depending on bowing parameters. We examine that the Bi inclusion affects the valance band and the N inclusion affects the conduction band of the host GaAs.

2. Method of calculation

The structural and electronic property calculations of $GaAs_{1-x}Bi_x$ and $GaAs_{1-x}N_x$ ternary alloys were performed in the framework of Density Functional Theory (DFT) [6], [7]. The theoretical calculations of ternary alloys were carried out using the plane wave self-consistent field (PWSCF) [8] code based on the plane wave pseudo potential method. The Zinc-Blende (ZB) model is used in all studied alloys. The exchange and correlation effects were treated using the generalized gradient approximation (GGA) [9] and the local density approximation (LDA) [10] for the self-consistent calculations. For our calculated alloys, the wave functions are expanded in the plane waves with the kinetic energy cutoff of 80 Ry. The charge density energy cutoff is 360 Ry. Geometry optimization of $GaAs_{1-x}N_x$ alloys are performed with symmetry P1 with 8-atom 1x1x1 simple cubic supercell. For $GaAs_{1-x}N_x$ alloys, the cubic unit cell is constructed with four Ga atoms and four Group V atoms (As/N) as follows coordinates:
Ga: (0.00 0.00 0.00), (0.50 0.50 0.00), (0.50 0.00 0.50), (0.00 0.50 0.50)
As/N: (0.25 0.25 0.25), (0.75 0.75 0.25), (0.75 0.25 0.75), (0.25 0.75 0.75)
Briefly, we have used 8 atoms simple cubic supercell for $GaAs_{1-x}N_x$ alloys.
On the other hand for $GaAs_{1-x}Bi_x$ alloys, for more detailed investigation of the band gap energies, the geometry optimization is performed with symmetry F-43m with 16 atoms 2x2x2 face centered cubic supercell. The 2x2x2 supercell of $GaAs_{1-x}Bi_x$ is constructed with 8 Ga atoms and 8 Group V atoms (As/Bi) as indicated coordinates below:
Ga: (0.00 0.00 0.00), (0.00 -0.00 0.50), (-0.00 0.50 0.00), (-0.00 0.50 0.50), (0.50 0.00 0.00), (0.50 0.00 0.50), (0.50 0.50 0.00), (0.50 0.50 0.50)
As/Bi: (0.1250 0.1250 0.1250), (0.1250 0.1250 0.6250), (0.1250 0.6250 0.1250), (0.1250 0.6250 0.6250), (0.6250 0.1250 0.1250), (0.6250 0.1250 0.6250), (0.6250 0.6250 0.1250), (0.6250 0.6250 0.6250)
In this study, Brillouin Zone (BZ) integrations were performed using 4×4×4 k-point meshes for all x compositions. For the calculation of the bulk properties in the ZB phase, we evaluated the total energy as a function of lattice constant.

3. Results and discussions

3.1. Structural properties

In this section, the calculations were firstly carried out to determine the structural properties of $GaAs_{1-x}N_x$and $GaAs_{1-x}Bi_x$ ternary alloys. Geometry optimization of $GaAs_{1-x}N_x$ alloys are performed with symmetry P1 with 8-atom 1x1x1 simple cubic supercell. And, in $GaAs_{1-x}Bi_x$ alloys, the geometry optimization is performed with symmetry F-43m with 16 atoms 2x2x2 face centered cubic supercell for more detail investigation of the band gap energies,. The supercell for $GaAs_{1-x}N_x$ ternary alloys could obtain 0.000, 0.250, 0.500, 0.750 and 1.000 values for x concentration. And, for more detail investigation, the supercell for $GaAs_{1-x}Bi_x$ ternary alloys could obtain 0.000, 0.125, 0.250, 0.375, 0.500, 0.625, 0.750, 0.875 and 1.000 values for x concentration. We have summarized the calculated lattice parameter of binary (GaAs, GaN, GaBi) and ternary in order to save some spaces only of x=0.5 alloys ($GaAs_{0.5}N_{0.5}$ and $GaAs_{0.5}Bi_{0.5}$) with other theoretical and experimental data in Table 1. In reference to our results, lattice parameter of the binary compounds (GaAs, GaN, GaBi) shows deviation 0.2% and 6% with other theoretical [12,16] and experimental [14,17] values. On the other hand, for $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ ternary alloys, the deviation of lattice parameter is around 2% as shown in Table 1.

We have plotted the calculated lattice parameter values of $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ ternary alloys as a function of x concentration in Figure 1. As shown in Figure1, lattice constant increases almost linearly when Bi concentration is increased, besides that it decreases also almost linearly when N concentration increases.

Table 1: Calculated Equilibrium Lattice Constants 'a' with Results of other Theoretical and Experimental Studies.

Material	a (Å)	Reference
GaN	4.55 (GGA) 4.43 (LDA) 4.48 4.50	Our work Our work Theory [11] Theory [12]
$GaAs_{0.5}N_{0.5}$	5.28 (GGA) 5.08 (LDA) 5.18	Our work Our work Theory [11]
GaAs	5.53 (GGA) 5.55 (LDA) 5.54 5.64	Our work Our work Theory [13] Expt. [14]
$GaAs_{0.5}Bi_{0.5}$	5.68 (GGA) 5.99	Our work Theory [15]
GaBi	5.94 (GGA) 6.17 6.32	Our work Theory [16] Expt. [17]

According to the Vegard's law [18] the lattice constant varies linearly with composition x:

$$a\ (AB_{1-x}C_x) = (1-x)aAB + (x)aAC \quad (1)$$

aAB and aAC are the equilibrium lattice constants of binary AB and AC, respectively, and $a(AB_{1-x}C_x)$ is the alloy lattice constant. The lattice constant of $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ can be approximated using the formula (1):

$$a\ (GaAs_{1-x}N_x) = (1-x)aGaAs + (x)aGaN \quad (2)$$

$$a\ (GaAs_{1-x}Bi_x) = (1-x)aGaAs + (x)aGaBi \quad (3)$$

As shown in Figure 1, the calculated lattice constants are linearly with compositions x, as indicated in Vegard's law.

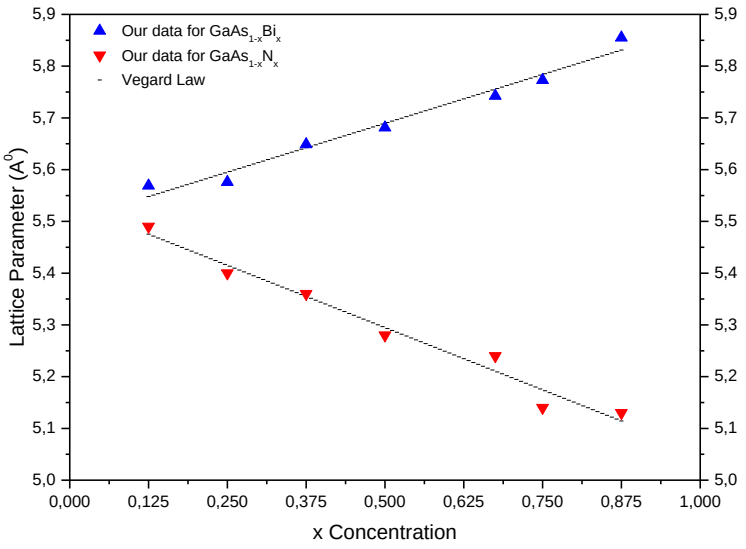

Fig. 1: Calculated Equilibrium Lattice Constants of $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ for Various x Concentrations.

3.2. Electronic properties

Electronic band structures of the studied alloys were obtained using the calculated lattice constants at the equilibrium. Figure 2 presents the electronic band structures for ZB phase of GaN, GaAs and $GaAs_{0.5}Bi_{0.5}$ compounds along with the high symmetry directions. The band structures of ternary $GaAs_{1-x}Bi_x$ alloys that are given in Figure 3 are only for a few x compositions in order to save some spaces.

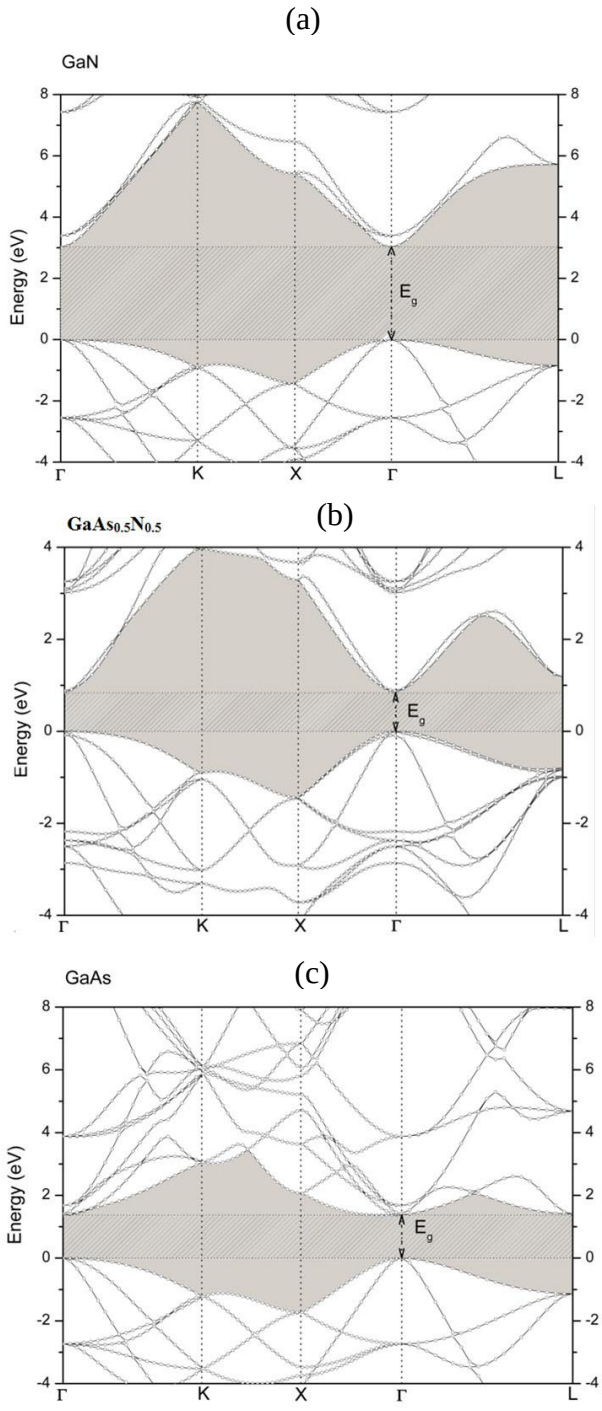

Fig. 2: Electronic Band Structure of **a)** GaN, **b)** $GaN_{0.5}As_{0.5}$ and **c)** GaAs. The Fermi Level is adjusted as the Zero Energy Level.

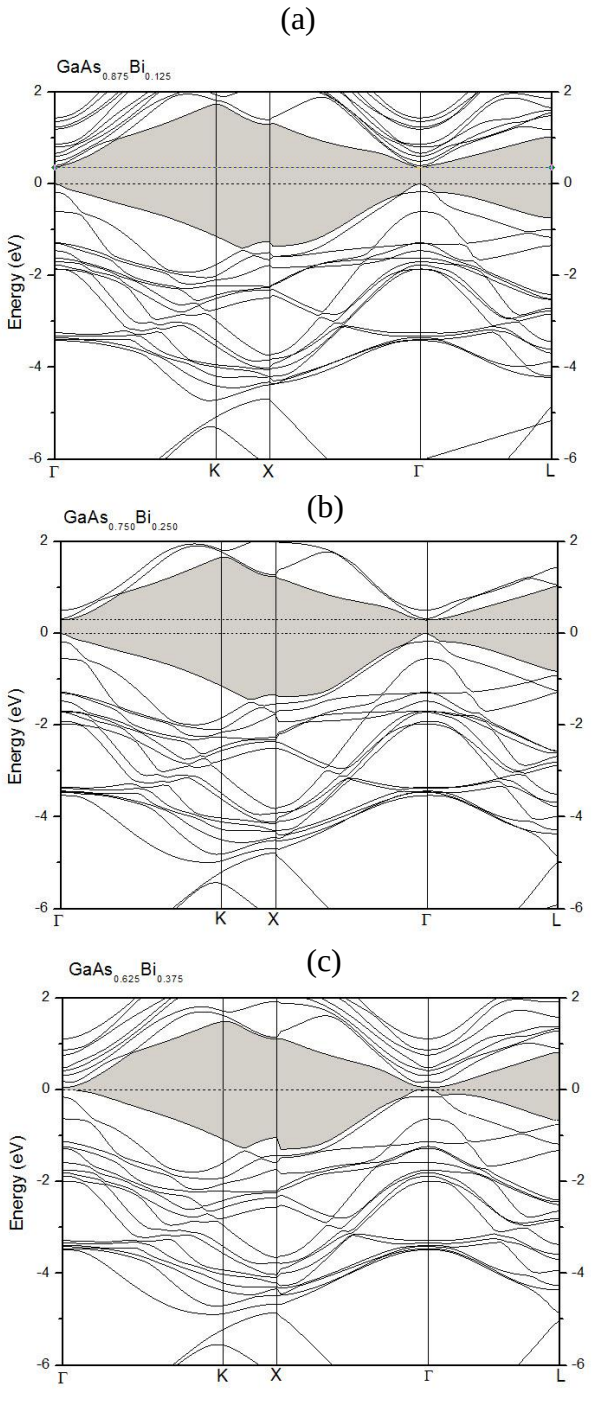

Fig. 3: Electronic Band Structure of **a)** $GaAs_{0.875}Bi_{0.125}$, **b)** $GaAs_{0.750}Bi_{0.250}$ and **c)** $GaAs_{0.625}Bi_{0.375}$. The Fermi Level is adjusted as the Zero Energy Level.

As shown in Figure 2 and 3 these compounds are direct band gap semiconductors with the minimum of conduction band at Γ symmetry point at the center of Brillouin region. In Table 2, we summarized the band gap energies for the studied materials. Our results are parallel to the theoretical [12], [19] and experimental [20-23] values.

The band gap energy of $GaAs_{1-x}N_x$ shows unexpected and drastic decrease with increasing N concentration in low N composition region and shows a nonlinear tendency for whole N concentration. This nonlinearity is related to gap bowing. In order to determine that nonlinear behavior, we calculated the bowing parameter for GaAsN and GaAsBi alloys by using the following equation:

$$b = \frac{\left| E_g(AB_{1-x}C_x) - (1-x)E_g AB - xE_g AC \right|}{x(1-x)} \quad (4)$$

Table 2: Calculated Band Gap Energies with Results of other Theoretical and Experimental Studies.

Material	E_g (eV)	Reference
GaN	3.0267 3.2-3.3 3.3	Our work Theory [12] Expt. [21-23]
$GaAs_{0.5}N_{0.5}$	0.8414	Our work
GaAs	1.3799 (GGA) 1.2 (LDA) 1.18(GGA) 1.12(LDA) 1.424	Our work Our work Theory [24] Theory [24] Expt. [20]
$GaAs_{0.875}Bi_{0.125}$	0.3831	Our work
$GaAs_{0.75}Bi_{0.25}$	0.2874	Our work
$GaAs_{0.625}Bi_{0.375}$	0.0478	Our work

Where the curvature b is generally known as gap bowing parameter. The results of bowing parameter are presented in Table 3. Our results are in good agreement with theoretical [25] values for $GaAs_{1-x}N_x$ ternary alloys. In Figure 4, we drew the graph of equation b and obtain the fit equation for both alloys.

Using the Allometrik Fit equations, we have presented the band gap energies of $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ as a function of lattice parameter in Figure 5. As shown in Figure 5, for low N concentration the band gap energy shows unexpected behavior and decreases dramatically. After the minimum value, the band gap energy increases almost linearly with increasing N concentration as expected. Again from the Figure 5, the band gap energy of $GaAs_{1-x}Bi_x$ decreases nonlinearly with increasing Bi concentration. Over around %40 concentration of Bi (x>0.4), the behavior of $GaAs_{1-x}Bi_x$ alloy becomes metallic.

The alloy of $GaAs_{1-x}N_x$ which include N in place of As in GaAs, perturbs the conduction band as in Figure 6. Changing of N concentration caused effective variation on conduction band minimum at Γ point. However the effect of Nitrogen incorporation to valance band is very weak as shown in Figure 6.The bismuth alloy $GaAs_{1-x}Bi_x$ is complementary to nitrides because incorporating Bi in GaAs perturbs the valence band, whereas N in GaAs perturbs the conduction band as shown in Figure 7.

Table 3: Bowing Parameter Data for $GaAs_xN_{1-X}$ and $GaAs_xBi_{1-X}$ for Different x Concentration.

Material	Bowing Parameter (eV)	Reference
Ga $As_{0.75}N_{0.25}$	7.96267 7.6	Our work Theory [25]
Ga $As_{0.50}N_{0.50}$	5.44760 6.84	Our work Theory [25]
Ga $As_{0.25}N_{0.75}$	4.66187	Our work
$GaAs_{0.875}Bi_{0.125}$	5.94	Our work
$GaAs_{0.75}Bi_{0.25}$	3.27	Our work
$GaAs_{0.625}Bi_{0.375}$	2.99	Our work
$GaAs_{0.50}Bi_{0.50}$	2.4	Our work

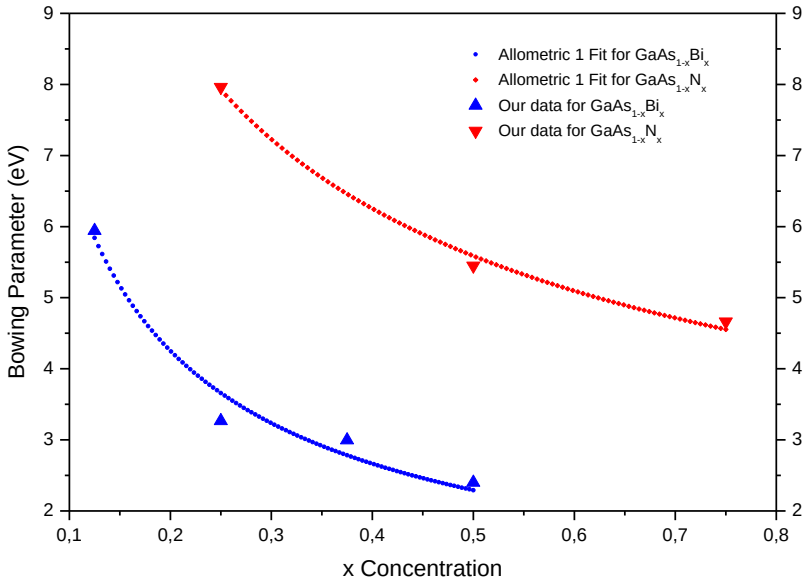

Fig. 4: Bowing Parameter of $GaAs_{1-X}N_x$ and $GaAs_{1-X}Bi_x$ as a Function of x Concentration.

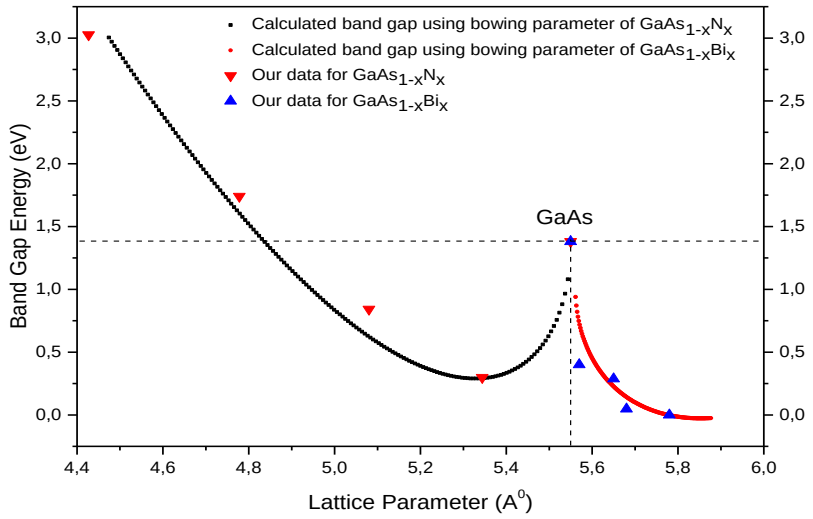

Fig. 5: Band Gap Energies of $GaAs_{1-X}N_x$ and $GaAs_{1-X}Bi_x$ as a Function of Lattice Parameter.

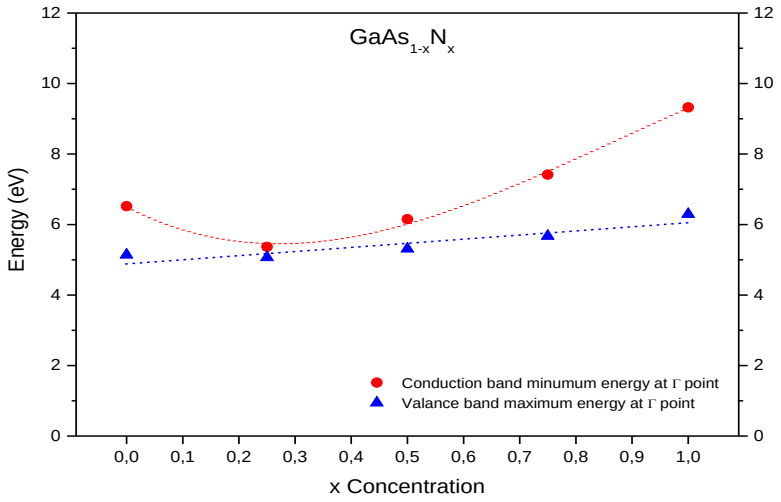

Fig. 6: Conduction Band Minimum Energy and Valance Band Maximum Energy of $GaAs_{1-X}N_x$ with Different N Concentrations.

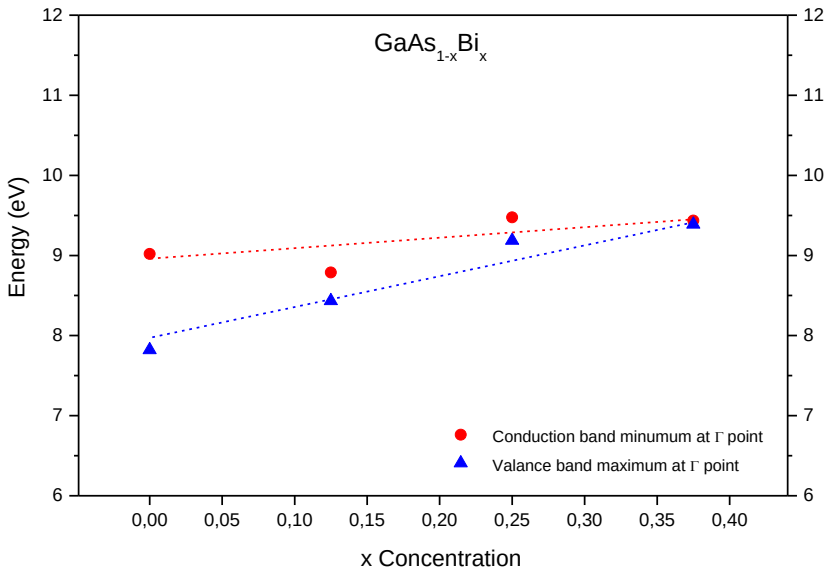

Fig. 7: Conduction Band Minimum Energy and Valance Band Maximum Energy of $GaAs_{1-X}Bi_x$ with Different Bi Concentrations.

4. Conclusions

We used the first principle pseudo potential method which is based on DFT within LDA and GGA to calculate the structural and electronic properties of binary (GaN, GaAs, GaBi), ternary ($GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$) alloys. We calculated the equilibrium lattice constants and band gap energies. The composition dependence of lattice constant is found to be linear behavior as indicated in Vegard's law. On the other hand, composition dependent band gaps have nonlinear behavior in both ternary alloys with different bowing parameters. All of the calculated materials are characterized by direct band gap along the Γ direction. Both alloys show a giant band gap bowing effect in which a small amount of element Bi which perturbs the valance band or N which perturbs the conduction band causes a large reduction in the band gap. The results of our structural and electronic properties are in good agreement with other theoretical and experimental values. We expect that, from this work the obtained results and especially graphics will be tested, to confirm their reliability, in future theoretically, experiments and with different methods.

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