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Structural and electronic properties of $Ga_{1-x}In_x As_{1-y}N_y$ quaternary semiconductor alloy on GaAs substrate

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ABSTRACT

We have presented structural and electronic properties of binary (GaAs, GaN and InAs), ternary ($Ga_{1-x}In_xAs$ and $GaAs_{1-y}N_y$) and quaternary ($Ga_{1-x}In_xAs_{1-y}N_y$) semiconductor alloys by using a first-principles pseudopotential technique. The structural and electronic properties of Zinc-Blende phase of these materials have been calculated by using the local density approximation (LDA) of the density-functional theory (DFT). To obtain the lattice parameter and band gap energy of the (GaInAsN) quaternary semiconductor alloy we separately calculated the lattice constant and band gap energies of ternary semiconductor alloys, namely GaAsN and GaInAs. The calculated lattice constant, bulk modulus and the direct band gaps for studied semiconductors showed great parallelism with the previous available theoretical and experimental studies.

1. Introduction

It is a well known fact that, semiconductor heterostructures are now widely used in electronics and optoelectronic device technology. In general, heterostructures are produced to form low dimensional electronic systems such as quantum wells (QWs) or quantum dots (QDs) by confining electrons and holes. Low dimensional systems are attractive for many applications thanks to their high carrier concentration and other electronic properties, which are formed by heterojunctions.

Nitrogen (N) inclusive III–V semiconductor heterostructure alloys provide opportunities to engineer material properties and they are also suitable for a variety of electronic and optoelectronics device applications. For instance, diode lasers [1], photodetectors [2], multijunction high efficiency solar cells [3], vertical cavity surface emitting lasers [4], vertical external-cavity surface emitting lasers [5], and semiconductor optical amplifiers [6] are only a few of the devices they used. However, the presence of nitrogen atoms into III–V lattice makes it difficult to obtain high quality materials due to the dissimilarities in atomic radius and electro-negativities between N and replaced atoms of host semiconductor. These dissimilarities in atomic radius and electro-negativities generate point defects. Therefore, the optical and electrical properties are strongly affected by the presence of the N atoms.

Another defect while trying to produce heterojunctions is that the thin overlayer causes the built-in strain if a semiconductor with mismatched lattice is grown on a substrate. After critical thickness, it will eventually be favorable for the overlayer to generate line defect which is called dislocation. These additional build-in strain and dislocation have important effects on mechanic, electronic and optoelectronic properties of the material. And also, the performance of the devices is negatively affected by deterioration of the periodic potential in the lattice.

During the past few decades, dilute nitrides, especially the GaInAsN on GaAs substrate's quaternary material system, have attracted a great deal of attention of the scientists. Potential applications of the GaInAsN on GaAs substrate in a variety of optoelectronic devices have made the dilute nitrides attractive materials thanks to the large conduction band offset and unusual physical properties such as high electron confinement in the QWs [7,4].

In this study, we have investigated the electronic and structural properties of GaInAsN with the help of the density function theory. We have examined the lattice constant and band gap energy of ternary GaInAs, GaAsN, and quaternary GaInAsN alloys separately, by using different In and N concentrations.

2. Method of calculation

The structural and electronic properties of ternary $Ga_{1-x}In_xAs$, $GaAs_{1-y}N_y$ and quaternary $Ga_{1-x}In_xAs_{1-y}N_y$ semiconductor alloys are investigated using the PWSCF [8] code based on the plane-wave pseudopotential method. The Zinc-Blende (ZB) model is used in all studied alloys. We have used the first-principles method based on density functional theory (DFT) [9,10] for the theoretical calculations. The local density approximation (LDA), which is combined with the plane wave pseudopotential approach, supplied an easy system whose certainty and predictive ability for structural and electronic properties have been presented in a vast type of framework. For this reason, we used the DFT and pseudopotential method within the

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Table 1
Calculated equilibrium lattice constants (a) and bulk modules (B) with results of other theoretical and experimental studies.

Material	a (Å)	B (GPa)	Reference
GaN	4.427	207.4	This work
	4.480	192.6	Theory [14]
	4.500	–	Theory [20]
$Ga\ As_{0.50}N_{0.50}$	5.080	103.5	This work
	5.175	106.6	Theory [14]
$Ga_{0.50}In_{0.50}\ As_{0.50}N_{0.50}$	5.321	102.3	This work
GaAs	5.551	73.70	This work
	5.580	74.53	Theory [18]
	5.540	77.10	Theory [13]
	5.640	77.00	Expt. [16]
$Ga_{0.50}In_{0.50}As$	5.791	68.30	This work
	5.820	66.45	Theory [18]
InAs	5.956	65.70	This work
	6.191	48.68	Theory [15]
	6.058	–	Expt. [17]
InN	4.957	183.3	This work
	4.980	–	Theory [20]

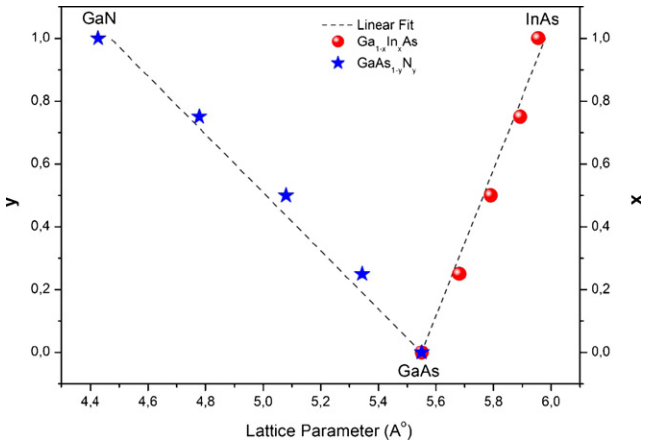

Fig. 1. Calculated equilibrium lattice constants of $Ga_{1-x}In_xAs$ and $GaAs_{1-y}N_y$ for various x and y concentration.

LDA approach in finite supercell to exemplify the crystal. The exchange correlation energy was parameterized by Perdew and Zunger [11]. For our calculated alloys, the wave functions are expanded in the plane waves with the kinetic energy cutoff of 25 Ry. The charge density energy cutoff is 100 Ry. A cubic unit cell is constructed with four atom Group III atoms (Ga/In) and four Group V atoms (As/N). We replaced one, two and three Ga atoms, respectively, by In to get the desired concentration. And, As atoms were replaced by N atoms like Ga/In replacement. In real crystal lattice, it is also possible N–N or other pairs and unwanted bonds while growing the structure. In our work, we neglected this kind of pairs and bonds and we assumed that all superlattices which produce the structure are equal.

In this study, Brillouin Zone (BZ) integrations were performed using $4 \times 4 \times 4$ $\vec{k}$ -point meshes for all x and y compositions. For the calculation of the bulk properties in the ZB phase, we evaluated the total energy as a function of lattice constant. The bulk modulus B was obtained by fitting the numerical data to Murnaghan's equation of state [12] around the region of the minimum total energy. The structural properties of the calculated materials were studied by using the first-principles pseudopotential method.

For all studied materials (binary, ternary and quaternary), the geometrical arrangement of Ga–In and As–N atoms were determined randomly by pwscf code. We used cubic super cell to compute the structural and the electronic properties of calculated semiconductors. These atoms were placed as following positions:

$$\text{Ga/In}: 000, 0\,\frac{1}{2}\,\frac{1}{2}, \frac{1}{2}\,0\,\frac{1}{2}, \frac{1}{2}\,\frac{1}{2}\,0$$

$$\text{As/N}: \frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}, \frac{1}{4}\,\frac{3}{4}\,\frac{3}{4}, \frac{3}{4}\,\frac{1}{4}\,\frac{3}{4}, \frac{3}{4}\,\frac{3}{4}\,\frac{1}{4}$$

By means of the pwscf code, we calculated the equilibrium lattice constant, bulk modulus and the direct energy gap (E_g) at the Γ point.

Primarily, equilibrium lattice parameters for the studied materials in ZB structure were calculated by minimization of the crystal's total energy to its volume. Then, the equilibrium lattice constant and the bulk modulus were obtained from the minimization curves by fitting to the Murnaghan equation of state [12]. And finally, the band structures, at the equilibrium lattice constant for studied materials, calculated along the high-symmetry directions in the simple-cubic BZ.

3. Results and discussion

3.1. Structural properties

We have summarized the calculated structural properties (lattice parameter and bulk modules) of binary (GaAs, InAs, GaN, and InN), ternary ($GaAs_{1-y}N_y$ and $Ga_{1-x}In_xAs$) and quaternary ($Ga_{1-x}In_xAs_{1-y}N_y$) alloys with other theoretical and experimental data in Table 1. In our work, we used 8 atom simple cubic $1 \times 1 \times 1$ supercell for our theoretical calculation. The supercell for $A_{1-x}B_xC_{1-y}D_y$ quaternary or ternary ($AC_{1-y}D_y$, $A_{1-x}B_xC$) alloys could only obtain 0, 0.25, 0.50, 0.75, and 1 values for x and y. We have provided the results for only given x and y 0.5 composition to save some space on our study. In reference to our results, lattice parameter of the binary compounds (GaAs, InAs, GaN and InN) shows deviation between 0.2% and 1.5% with other theoretical [13–15] and experimental [16,17] values. Otherwise, compared to theoretical [14,18] values, the lattice parameters of $Ga_{1-x}In_xAs$ and $GaAs_{1-y}N_y$ were found less than 0.5% and 1.2%, respectively. In this study, the calculated bulk modulus of all studied alloys for x and y equaled 0.5 composition are also presented in Table 1. Our results are in good agreement with other works [13–16,18]. The compressibility of the crystal structure decreased when In concentration increased. However increase of N concentration caused the compressibility of the crystal structure to increase. This situation causes a change in bulk modulus, due to the atomic mass difference between replaced atoms. The bulk modules decrease from GaN to InAs, namely from the lower to higher atomic numbers. The compressibility change occurs in the following sequence:

$$B_{GaN} > B_{GaAs_{0.5}N_{0.5}} > B_{GaAs} > B_{Ga_{0.5}In_{0.5}As} > B_{InAs} \quad (1)$$

This result shows that InAs is more compressible than GaAs, and also GaAs is more compressible than GaN.

For quaternary alloy $Ga_{1-x}In_xAs_{1-y}N_y$, as far as we are concerned, there is no experimental and theoretical value for structural properties. But, we demonstrated the structural properties of $Ga_{1-x}In_xN_yAs_{1-y}$ using ternary alloys. In Fig. 1, the lattice constant results are plotted as a function of x and y composition. As shown in Fig. 1, lattice constant increases almost linearly when In composition is increased, besides that it decreases also almost linearly when N composition increases. These increase and decrease give us the difference lattice constant of alloy than GaAs thus we demonstrated in Fig. 2. As shown in Fig. 2, the concentration of N in GaInAsN quaternary alloy caused compression and the concentration of In caused expansion on the lattice constant of GaInAsN.

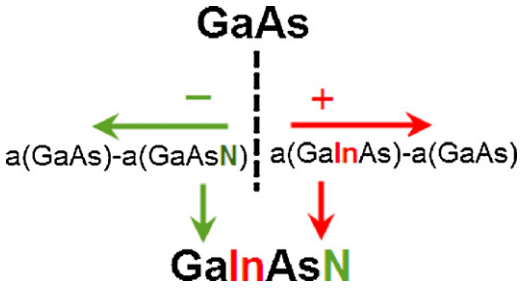

Fig. 2. Demonstration of lattice parameter of GaInAsN alloy.

Table 2
Band gap energies for studied materials.

Material	E_g (eV)	Reference
GaN	3.0267	This work
	3.2–3.3	Theory [20]
	3.3	Expt. [23–25]
$GaN_{0.50}As_{0.50}$	0.8414	This work
$Ga_{0.50}In_{0.50}As_{0.50}$ $N_{0.50}$	0.3387	This work
GaAs	1.3799	This work
	1.424	Expt. [22]
$Ga_{0.50}In_{0.50}As$	0.5966	This work
InAs	0.4114	This work
	0.34	Theory [21]
	0.416	Expt. [26]

The lattice constant of $A_{1-x}B_xC_{1-y}D_y$ quaternary alloy is determined by using Vegard's law [19] as follows:

$$a_{ABCD}(x,y) = xya_{BD} + (1-x)_{ya}AD + x(1-y)a_{BC} + (1-x)(1-y)a_{AC} \quad (2)$$

When we used the composition ratio x and y and ordered Eq. (2) we obtained the lattice constant of $Ga_{1-x}In_xAs_{1-y}N_y$ alloy as follows depending on Vegard's law:

$$a_{GaInAsN}(x,y) = xya_{InN} + (1-x)ya_{GaN} + x(1-y)a_{InAs} + (1-x)(1-y)a_{GaAs} \quad (3)$$

The lattice constant of GaInAsN which we obtained from Eq. (3) overlaps with the calculated lattice constant of GaInAsN for the same In and N concentrations. With respect to the above mentioned formula, the lattice parameter of $Ga_{0.5}In_{0.5}As_{0.5}N_{0.5}$ is about 2% less than our calculated results as shown in Table 1. These results show us that, Eq. (3) is applicable for the lattice constant of $Ga_{1-x}In_xN_yAs_{1-y}$ for all different In and N concentrations.

Our results for ternary alloys have also been examined by the validity of virtual crystal approximation. According to the Vegard's law [19] the lattice constant varies linearly with composition x.

$$a(A_xB_{1-x}C) = xa_{AC} + (1-x)a_{BC} \quad (4)$$

a_{AC} and a_{BC} are the equilibrium lattice constants of binary AC and BC, respectively, and $a(A_xB_{1-x}C)$ is the alloy lattice constant. The lattice constant of $Ga_{1-x}In_xAs$ and $GaAs_{1-y}N_y$ can be approximated by using the above mentioned Eq. (4):

$$a(Ga_{1-x}In_xAs) = xa_{InAs} + (1-x)a_{GaAs} \quad (5)$$

$$a(GaAs_{1-y}N_y) = ya_{GaN} + (1-y)a_{GaAs} \quad (6)$$

In Fig. 1, the calculated lattice constants are linear with compositions x and y, therefore our calculations are consistent with the Vegard's law.

3.2. Electronic properties

Electronic band structures of the studied alloys were obtained using the calculated lattice constants at the equilibrium. Fig. 3 presents the electronic band structures for ZB phase of binary (GaAs, InAs, and GaN) compounds along with the high symmetry directions. The band structures of ternary ($Ga_{1-x}In_xAs$ and $GaAs_{1-y}N_y$) and quaternary ($Ga_{1-x}In_xAs_{1-y}N_y$) alloys that are given in Fig. 4 are only for $x = 0.5$ and $y = 0.5$ compositions in order to save some spaces. As shown in Figs. 3 and 4 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 were parallel to the theoretical [20,21] and experimental [22–25] values. The band gap energy of $GaAs_{1-y}N_y$ 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 different N concentrations by using the following equation:

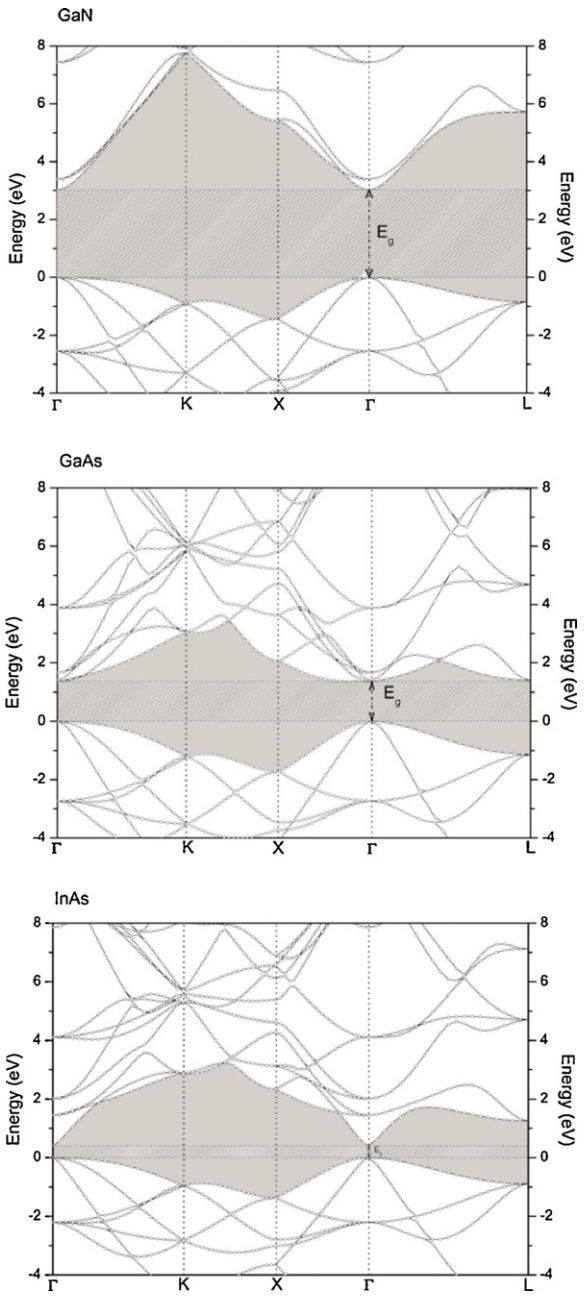

Fig. 3. Electronic band structure of GaN, GaAs and InAs, respectively. The Fermi level is adjusted as the zero energy level.

$$E_g(AB_{1-y}C_y) = yE_gAC + (1-y)E_gAB - y(1-y)b \quad (7)$$

for $GaAs_{1-y}N_y$

$$E_g(GaAs_{1-y}N_y) = yE_gGaN + (1-y)E_gGaAs - y(1-y)b \quad (8)$$

where the curvature b is generally known as gap bowing parameter.

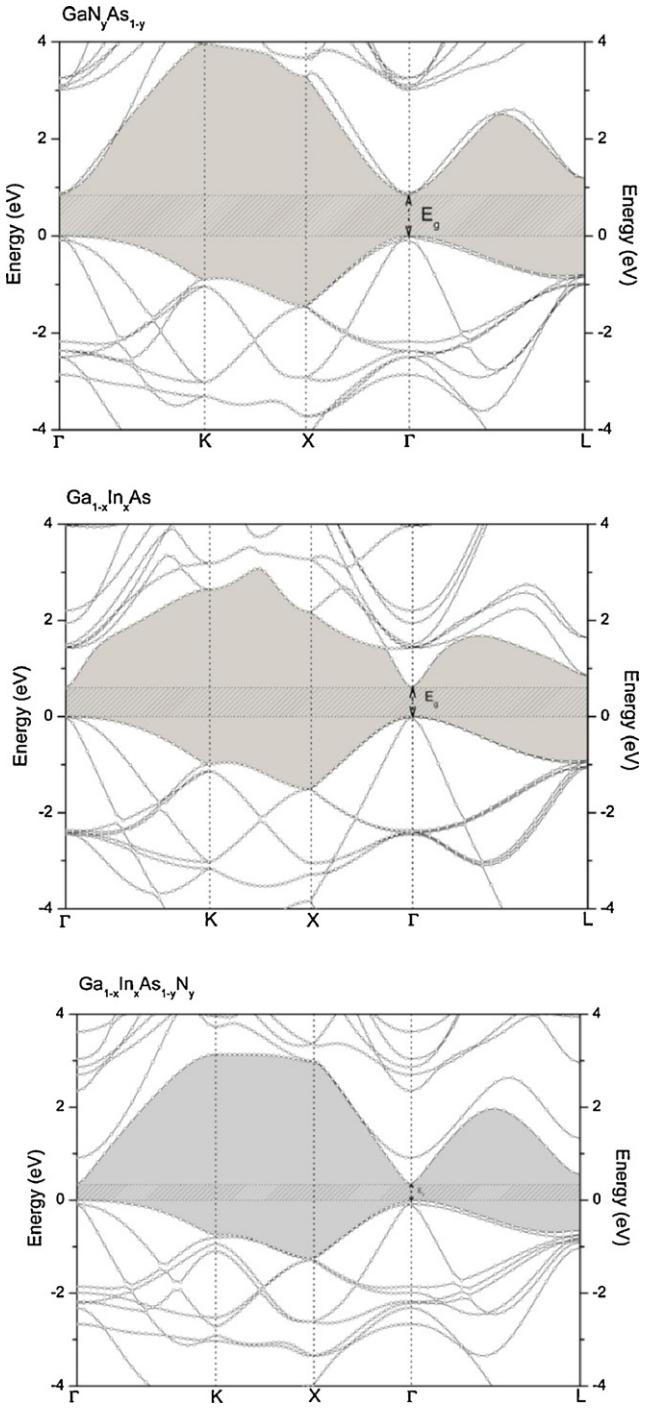

Fig. 4. Electronic band structure of ternary $Ga_{1-x}In_xAs$ and $GaAs_{1-y}N_y$, and quaternary $Ga_{1-x}In_xAs_{1-y}N_y$ alloys for $x = 0.5$ and $y = 0.5$ compositions. The Fermi level is adjusted as the zero energy level.

By means of Eq. (8), we obtained the bowing parameter as follows:

$$b = \frac{|E_g(GaAs_{1-y}N_y) - yE_g(GaN) - (1-y)E_g(GaAs)|}{y(1-y)} \quad (9)$$

The results of bowing parameter are presented in Table 3. Our results are in good agreement with theoretical [27] values.

We drew the graph of equation b in Fig. 5. We fitted the data of bowing parameter by using following nonlinear curve fit equation:

$$b = C \cdot y^D \quad (10)$$

Table 3
Bowing parameter data for $GaAs_{1-y}N_y$ for different y composition.

Material	Bowing parameter (eV)	Reference
Ga	7.93	This work
$As_{0.75}N_{0.25}$	7.60	Theory [27]
Ga	5.59	This work
$As_{0.50}N_{0.50}$	6.84	Theory [27]
Ga $As_{0.25}N_{0.75}$	4.55	This work

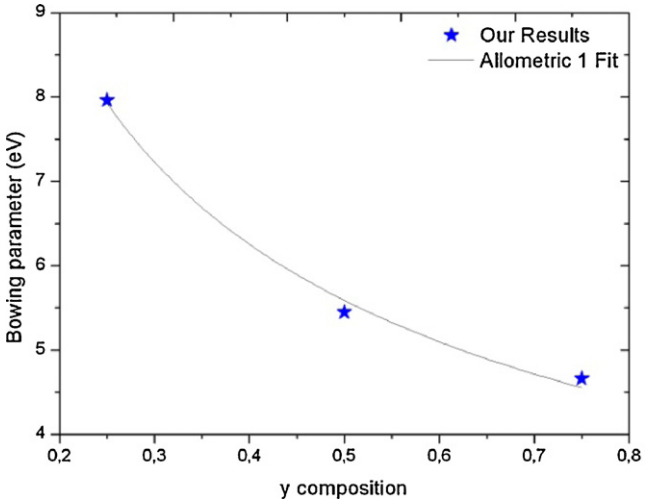

Fig. 5. Bowing parameter of $GaAs_{1-y}N_y$ as a function y composition.

From Eq. (10) we obtained $C = 3.93853$ and $D = -0.5045$ values after fitting.

Using Eq. (8), we have presented band gap energies of $GaAs_{1-y}N_y$ as a function of lattice parameter in Fig. 6. As shown in Fig. 6, 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 Fig. 6, the band gap energy of $Ga_{1-x}In_xAs$ decreases with increasing In concentration. Nevertheless there is small bent, only in a short range of low Ga concentration which is shown in GaInAs side of Fig. 6. With reference to Fig. 6, the bowing of $Ga_{1-x}In_xAs$ which caused the small bent is too much smaller than the bowing of $GaAs_{1-y}N_y$. For this reason, we conceded the band gap energy of $Ga_{1-x}In_xAs$ changes linearly with respect to $GaAs_{1-y}N_y$.

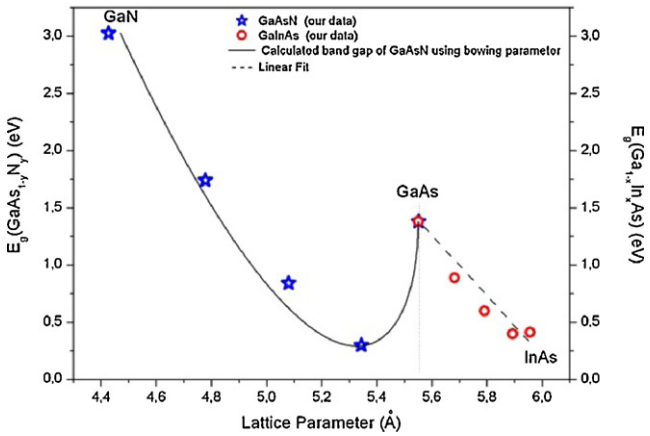

Fig. 6. Band gap energies of $Ga_{1-x}In_xAs$ and $GaAs_{1-y}N_y$ as a function lattice parameter.

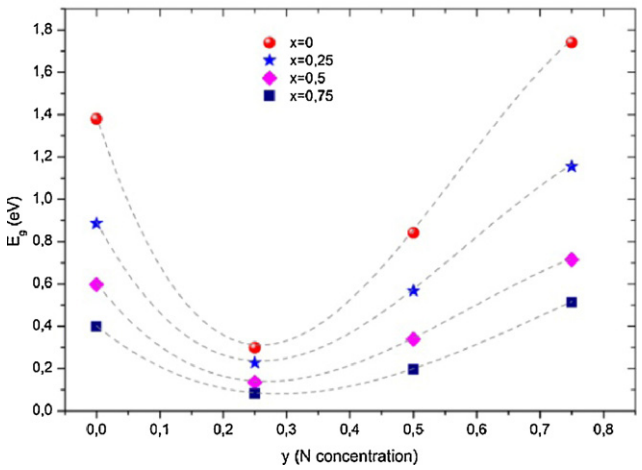

Fig. 7. Band gap energies of $Ga_{1-x}In_xAs_{1-y}N_y$ as a function of y (N concentration) and x (In concentration).

We calculated band gap energy of $Ga_{1-x}In_xAs_{1-y}N_y$ quaternary alloy for different In and N concentration and the results are shown in Fig. 7. As shown in Fig. 7, for low In concentration the band gap of the alloy has large bowing parameter compared to high In concentration. Furthermore, for constant N concentration, band gap of $Ga_{1-x}In_xAs_{1-y}N_y$ decreases almost linearly with increasing In concentration. According to Eq. (3) and Fig. 7 we calculated the lattice constant and the band gap energy of the quaternary GaInAsN alloy for various In and N concentrations.

4. Conclusions

We used the first principle pseudopotential method which is based on density functional theory (DFT) within the local density approximation (LDA) to calculate the structural and electronic properties of binary (GaAs, InAs, and GaN), ternary ($GaAs_{1-y}N_y$ and $Ga_{1-x}In_xAs$) and quaternary ($Ga_{1-x}In_xAs_{1-y}N_y$) alloys. We calculated the equilibrium lattice constants and bulk modulus. The composition dependence of lattice constant is found to be linear.

All of the calculated materials are characterized by direct band gap along the Γ direction. Also, the bowing parameters for $GaAs_{1-y}N_y$ were investigated. Our structural and electronic results are in good agreement with other theoretical and experimental values. From this work, we expect that the obtained results and especially graphics will be tested, to confirm their reliability, in future theoretically, experimentally and with different methods.

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