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Theoretical calculations on structural and electronic properties of BGaAsBi alloys

Metin Aslan[a], Battal G. Yalcin, Mehmet Ustundag, and Sadik Bagci

Sakarya University Science and Art Faculty, Physics Department, Esentepe 54187 Sakarya, Turkey

Abstract. The structural and electronic properties of cubic $B_xGa_{1-x}As_{1-y}Bi_y$ alloys with bismuth (Bi) concentration of 0.0625, 0.125, 0.1875 and 0.25 are studied with various boron (B) compositions by means of density functional theory (DFT) within the Wu-Cohen (WC) exchange correlation potential based on generalized gradient approximation (GGA). For all studied alloy structures, we have implemented geometric optimization before the volume optimization calculations. The obtained equilibrium lattice constants and band gap of studied quaternary alloys are investigated for the first time in literature. While the lattice constant behavior changes linearly with boron concentration, increasing small amount of bismuth concentration alter the lattice constant nonlinearly. The present calculation shows that the band gap decreases with increasing bismuth concentration and direct band gap semiconductor alloy became an indirect band gap with increasing boron concentration. From the band offset calculation we have shown that increasing B and Bi concentration in host GaAs reduced the valance band offset in a heterostructure formed by GaAs and studied alloys.

1 Introduction

In recent years, there is much interest in the characterization of GaAs based III-V semiconductor alloys because of their potential optoelectronic applications in various fields [1–3]. For developing the science and technology, people always try to broaden the applications of GaAs. Doping other elements is one of the most commonly used methods to broaden the application of semiconductor and performed by replacing a small amount of host atoms with other group III or V guest atoms in periodic table. In the last few years there has been a gained interest in the study of GaAsBi alloys [4–7]. Incorporation of bismuth (Bi) to GaAs is found to have a significant influence on electronic and optical properties. Many researchers have observed a huge reduction in the band gap by replacing As with Bi [8–10]. That is why $GaAs_{1-x}Bi_x$ has attracted a great deal of interest due to their significant potential applications in solar cells, optoelectronic devices, semiconductor lasers and optical detectors [11–13]. On the other side Bi is a large atom compared to As and that causes defects because of the forceful strain in the lattice of common substrate GaAs. The line defects caused by the additional guest atoms reduce the material quality. To avoid the forceful strain on GaAs substrate and enhance the material quality, another small atom needs to co-doping. Boron (B) is the smallest atom in group III. So it is a useful atom to reduce the increased lattice in III-V semiconductor alloys replacing with the other host group III atom. Hence,

the increased lattice with incorporation of Bi to GaAs is reduced by co-doping with B instead of Ga atom. In addition to these, B compounds offer new class of materials and may open new possibilities for band gap engineering in III-V related semiconductor materials. Here, we propose $B_xGa_{1-x}As_{1-y}Bi_y$ as a new candidate material for optoelectronic device applications with the potential to be grown lattice matched on GaAs and InP substrate with band gap below 1.4 eV.

The rest of the paper is organized as follows. In Section 2, the computational method used in the present work is described. Results and their discussion are presented in Section 3. Finally, a conclusion of the work is given in Section 4.

2 Method of calculation

The calculation of structural properties of $B_xGa_{1-x}As_{1-y}Bi_y$ quaternary alloys are based on DFT calculations performed with the WIEN2k [14] software package for quantum calculations. For structural properties the exchange – correlation potential was calculated using the generalized gradient approximation (GGA) in the new form proposed by Wu and Cohen (WC-GGA) [15] which is an improved form of the most popular Perdew-Burke-Ernzerhof (PBE-GGA) [16]. For the electronic properties modified Becke-Johnson (mBJ) potential [17] was chosen. This potential is used to improve the band gap obtained by the conventional DFT-based methods [18].

[a] e-mail: maslan@sakarya.edu.tr

We use an energy cut-off parameter RK_{max} (R is the average radius of the muffin-tin (MT) spheres and K_{max} is the cut-off for the wave function basis) of 7.5 and radii of 1.69, 2.19, 2.17 and 2.5 bohr for boron, gallium, arsenide and bismuth, respectively. The cut-off energy is set to –7 Ry for separating core from valance states. Inside the MT spheres, the angular momentum expansion is expanded up to $l_{max} = 10$. And, magnitude of the largest vector G is equal to 12 $Ry^{1/2}$ in charge density Fourier expansion. For a well force, charge convergence of crystal system is stable within less than 0.001 e. And, in the total energy between self-consistency cycles (SCF) was $<10^{-4}$ Ry. In the considered alloy structure, free coordinates of atoms were relaxed using the quantum-mechanical forces so residual forces on the ions were <1 mRy/bohr.

For accurate Brillouin Zone (BZ) integrations, the standard special k-points technique of Monkhorst and Pack (MP) [19] was used. The k-mesh sizes was a $5 \times 2 \times 2$ MP special points (12 special k-points in the irreducible wedge of the BZ) for each considered 32-atom $2 \times 2 \times 1$ supercell. As a function of volume, the total energies are computed to be obtained lattice parameter by fitting to the Murnaghan equation of state [20].

3 Results and discussions

3.1 Structural properties

The calculations were firstly carried out to determine the structural properties of $B_xGa_{1-x}As_{1-y}Bi_y$ alloys in zinc blende (ZB) phase which is found to be the ground state structure for boron-V and bismuth-III compounds [21]. We have used $2 \times 2 \times 1$ supercell with 32-atom for the crystal structure of quaternary $B_xGa_{1-x}As_{1-y}Bi_y$ alloys. For all studied alloy structures, we have implemented geometric optimization before the volume optimization calculations. In order to better understand the stability of the studied alloys, we have calculated the formation energy (FE) for various substitutionally doped systems by using the following relation:

$$
\begin{aligned}
FE = E\left(B_xGa_{1-x}As_{1-y}Bi_y\right) &- \{xE\left(B, bulk\right) \\
&+ (1-x)E\left(Ga, bulk\right) + (1-y)E\left(As, bulk\right) \\
&+ yE\left(Bi, bulk\right)\}
\end{aligned} \tag{1}
$$

where $E(B_xGa_{1-x}As_{1-y}Bi_y)$ is the total energy per unit cell and $E(A, bulk)$ presents the energy per atom of substance A. By means of equation (1), we have calculated the formation energy for different boron concentrations. The obtained results for various compositions of x are shown in Table 1. As shown in Table 1, negative values indicate that the doped structures are stable.

We have calculated equilibrium lattice constants of studied binary compounds and quaternary $B_xGa_{1-x}As_{1-y}Bi_y$ alloys for several x and y compositions. The equilibrium lattice constant of $B_xGa_{1-x}As_{1-y}Bi_y$ alloys according to B concentration with fixed Bi concentration of 0.0625, 0.125, 0.1875, and 0.25 are shown

Table 1. The formation energies in a 32 atom unit cell for various compositions of x.

$B_xGa_{1-x}As_{0.9375}Bi_{0.0625}$ x composition	Formation energy $(10^3$ Ry$)$
0.0625	–13.7446
0.125	–13.5467
0.1875	–13.3357
0.25	–12.4706

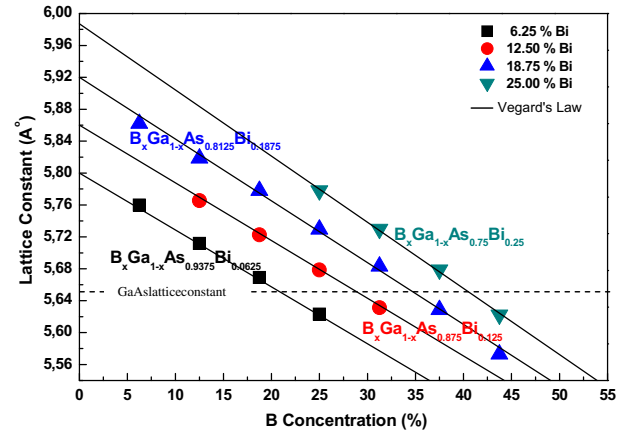**Fig. 1.** Lattice parameter of quaternary $B_xGa_{1-x}As_{1-y}Bi_y$ alloys versus boron concentrations for all calculated Bi compositions.

in Table 2. To our knowledge there are no theoretical and experimental results that have been published so far about the lattice constant of the studied alloys. The lattice constant of the alloys are reduced by increasing B concentration in given Bi composition as indicated in Table 2. In Figure 1, we have graphed the calculated lattice parameter of quaternary $B_xGa_{1-x}As_{1-y}Bi_y$ alloys versus B concentrations for different Bi (y) compositions. It is clearly seen that, the variation of calculated lattice constants by depending on B concentration is almost linear. It denotes that the lattice parameter of $B_xGa_{1-x}As_{1-y}Bi_y$ alloys versus B concentration excellently coincides with Vegard's law [22]. We have also presented lattice parameter of quaternary $B_xGa_{1-x}As_{1-y}Bi_y$ alloys according to Bi concentration with fixed B concentration at 25% in Figure 2. It is seen from this figure that there is non-linear increase of lattice constant with increasing Bi concentration. As indicated in Figure 2, there is high deviation from Vegard's law with small amount of Bi concentration. The non-linear behavior has been explained in various experimental [23,24] and theoretical [25,26] studies that the Vegard's law is not valid for the systems with strong lattice mismatched ternary alloys like GaAsBi.

3.2 Electronic properties

The calculation of the electronic band structure properties, magnitude of band gaps and density of states are carried out for BGaAsBi alloys in ZB structure at the calculated equilibrium lattice constant. The mBJ potential

Table 2. The equilibrium lattice constants of studied quaternary alloys.

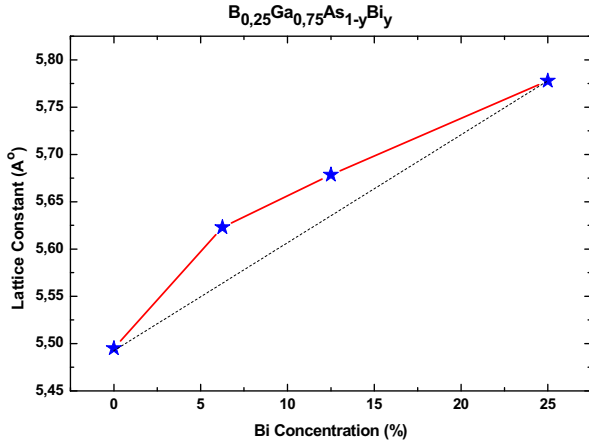| % 6.25 Bi		% 12.5 Bi		% 18.75 Bi		% 25 Bi	
$B_x Ga_{1-x} As_{0.9375} Bi_{0.0625}$		$B_x Ga_{1-x} As_{0.875} Bi_{0.125}$		$B_x Ga_{1-x} As_{0.8125} Bi_{0.1875}$		$B_x Ga_{1-x} As_{0.75} Bi_{0.25}$	
x concent. (%)	a (A°)	x concent. (%)	a (A°)	x concent. (%)	a (A°)	x concent. (%)	a (A°)
6.25	5.7600	12.50	5.7654	25.00	5.7296	25.00	5.7779
12.50	5.7117	18.75	5.7225	31.25	5.6831	31.25	5.7297
18.75	5.6690	25.00	5.6786	37.50	5.6287	37.50	5.6787
25.00	5.6231	31.25	5.6314	43.75	5.5729	43.75	5.6222

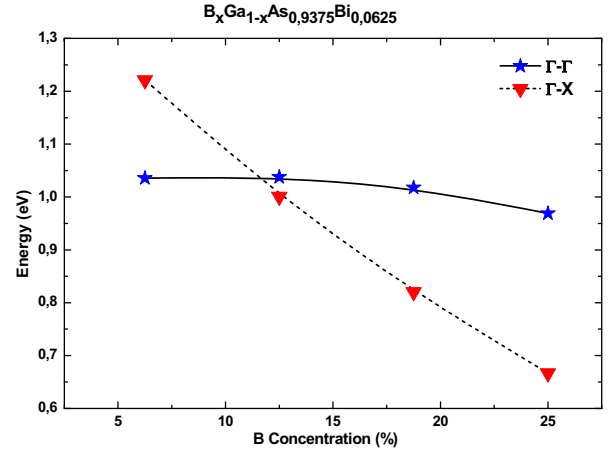**Fig. 2.** Non linear lattice constant behavior with small amount of Bi concentration.

Fig. 3. Direct to indirect band gap with increasing of B concentration.

Fig. 4. Schematic energy level diagram of conduction and valance band offsets of $B_{0.1875} Ga_{0.8125} As_{0.9375} Bi_{0.0625}$ and $B_{0.3125} Ga_{0.6875} As_{0.875} Bi_{0.125}$ on GaAs substrate.

which is more accurate than standard semi-local LDA and PBE-GGA calculations is chosen for the electronic calculations [27]. The transition energy at Γ-Γ and Γ-X of quaternary BGaAsBi alloys are given in Figure 3 for the fixed minimum Bi concentration of 6.25%. As indicated in Figure 3, up to about 12% of B concentration BGaAsBi alloy is a direct band gap semiconductor with the minimum of conduction band at Γ symmetry point. It can be easily seen from Figure 3 that Γ-X transition energy decreases with increasing of B concentration while Γ-Γ transition energy remains almost constant. If B concentration is increased above the specified value, then the BGaAsBi alloy became an indirect semiconductor. And the indirect band gap reduced with increasing B concentration in BGaAsBi alloy. From the band structure calculation we indicated that B atom pushed the X valley down, so direct band gap of BGaAsBi became an indirect band gap with increasing the B concentration as seen in Figure 3.

Determination the band offset between two semiconductors forming a heretostructure is one of the most fundamental properties of materials science. It is an important quantity to define the charge transport and quantum confinement. It has particular relation to design of light emitting diodes, multi junction solar cells, and other optoelectronic devices which feature an interface between two or more materials. Theoretical calculation has been performed to obtain the valance band offset of two compounds at their respective equilibrium position using the description (2) [28,29].
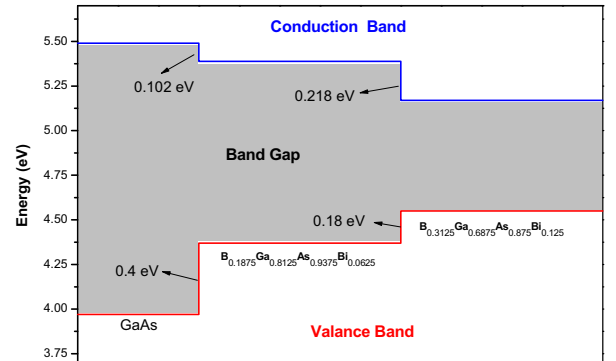
$$\Delta E_V(\text{AX/BY}) = \Delta E_{V,C'}(\text{BY}) - \Delta E_{V,C}(\text{AX}) + \Delta E_{C,C'}(\text{AX/BY}). \quad (2)$$

Here $\Delta E_{V,C}(\text{AX}) = E_V(\text{AX}) - E_C(\text{AX})$ is the energy difference between the valance band maximum (VBM) and the core level at the equilibrium lattice constant (the same for $\Delta E_{V,C'}(\text{BY})$). And $\Delta E_{C,C'}(\text{AX/BY}) = E_{C'}(\text{BY}) - E_C(\text{AX})$ is the core level energy difference between the two core levels in a relaxed (AX/BY) heterostructure. We have calculated the valance band and conduction band offsets between GaAs (AX) and $B_x Ga_{1-x} As_{1-y} Bi_y$ (BY) alloy which is lattice matched to GaAs. Figure 4 shows
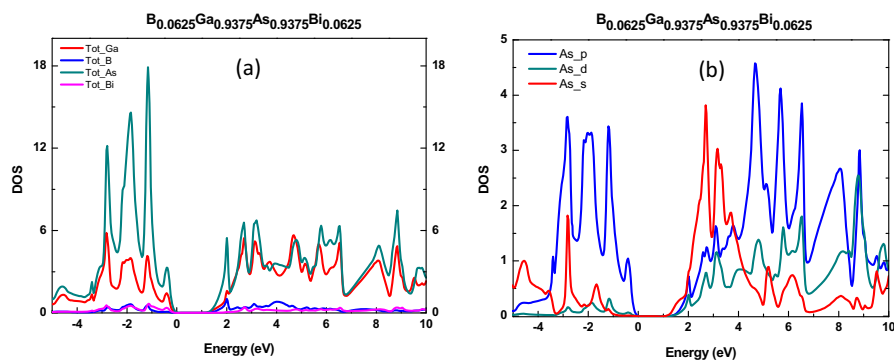
Fig. 5. (a) Total and (b) partial density of states of $B_{0.0625}Ga_{0.9375}As_{0.9375}Bi_{0.0625}$ alloy.

the schematic energy level diagrams which reduce the valance band offset with increasing of B and Bi concentration. Conversely, increasing the concentration of the guest atoms increases the conduction band offset as shown in Figure 4.

We also have calculated density of states (DOS) of the alloy presented in Figure 5 only for $x, y = 0.0625$ composition in order to save some spaces. We have found from the total density of states that As atom has dominant character near the valance band maximum as shown in Figure 5a. And we can identify that the p orbitals are more influential than the other orbitals from the partial density of states of As atom at the valance band maximum as indicated in Figure 5b.

4 Conclusion

We have calculated structural and electronic properties of $B_xGa_{1-x}As_{1-y}Bi_y$ semiconductor alloys as a new candidate material for optoelectronic device applications due to the potential to be grown lattice matched on GaAs and InP substrates with band gaps below 1.4 eV. From the structural calculations, we have found linear behavior with increasing B and non-linear behavior with increasing of Bi concentration of the alloy. From the band gap calculation, we have indicated that B atom pushed the X valley down, so direct band gap of $B_xGa_{1-x}As_{1-y}Bi_y$ became an indirect band gap with increasing of B concentration. We have also shown that conduction band offset increases with increasing of B and Bi concentration while valance band offset decreases. And finally from the DOS calculations we have found that the dominant effect comes from p orbitals of As atoms near the valance band maximum and s orbitals of As atoms near the conduction band minimum.

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