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Bismuth-containing semiconductors $GaAs_{1-x}Bi_x$ for energy conversion: Thermoelectric properties

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ABSTRACT

The electronic transport properties of $GaAs_{1-x}Bi_x$ alloys, are obtained using the semi-classical Boltzmann theory as incorporated in BoltzTraP code. The thermoelectric properties as a function of temperature at a constant value of chemical potential (μ) were calculated for the $GaAs_{1-x}Bi_x$ alloys at x = 0.0–1.0 with stepsize of 0.25. $GaAs_{1-x}Bi_x$ alloys are modeled using special quasi-random structures' (SQS) Zunger approach. The $GaAs_{1-x}Bi_x$ alloys have a direct band gap of 1.42 eV, 0.449 eV, 0.052 eV, 0.016 eV and −0.0056 eV for x = 0.0, 0.25, 0.50, 0.75 and 1.0, respectively. It is clearly seen that the energy gap decreases with increasing Bi concentration. The electronic band structures of $GaAs_{1-x}Bi_x$ alloys show that the bands are less dispersive for all high symmetry directions, suggesting that these alloys possess large effective mass for the carriers and hence a high thermopower. Calculation show that $GaAs_{0.75}Bi_{0.25}$ exhibits high carrier concentration and hence high electronic conductivity and power factor, whereas GaAs shows the highest value for Seebeck coefficient. GaBi exhibits the lowest values for most of the transport properties. The $GaAs_{1-x}Bi_x$ (x = 0.0, 0.25, 0.5, 0.75) alloys represents the p-type carrier except GaBi represent n-type at low temperate till 300 K then above this temperature it represents the p-type carrier. We should mention here the fluctuation in the values of σ/τ with changing the content of Bi atoms is attributed to the mobility and the concentration of the charge carrier. Finally substituting all As atoms by Bi atoms (GaBi) leads to reduce k_e/τ to lower than that of GaAs. $GaAs_{1-x}Bi_x$ alloys could be promising materials for thermoelectric applications due to the decrease in thermal conductivity with increasing x because bismuth is a heavy atom (better phonon scattering).

1. Introduction

$GaAs_{1-x}Bi_x$ alloys, as bismuth-containing semiconductors, have attracted a great deal of interest due to their significant potential applications in solar cells, optoelectronic devices, semiconductor lasers, and optical detectors [1]. It has been found that there is an influence on electronic and optical properties when GaAs is doped with Bi. Also there is a huge reduction in the band gap with replacing As by Bi [2] which is attributed to the fact that the size of Bi atom is much bigger than that of As atom. Therefore, with the substitution As by Bi, a compressive strain develops in the crystal [3–5], resulting in a significant modification in the electronic structure and hence in the optical and thermoelectric properties of the pristine alloys. The observed huge reduction in the energy band gap could be due to a resonant interaction between Bi *6p* state in the conduction band minimum (CBM) and the valence band maximum (VBM) [6–9]. The surfactant technology was successfully used to introduce Bi atom in GaAs compound [10]. This technology was totally different from the traditional molecular beam epitaxy (MBE) [11]. The resulting GaAsBi alloys are not traditional type of alloys due to the fact that Bi introduces bound states in addition to the bands, and behaves more like an isoelectronic donor rather than a true alloying element [6,7]. The growing demand for unusual thermoelectric materials motivated us to do a comprehensive investigation for the transport properties of $GaAs_{1-x}Bi_x$ Alloys.

Recently Alhassan et al. [12] have employed the Current-Voltage (I–V), Capacitance-Voltage (C–V), Deep Level Transient Spectroscopy (DLTS), Laplace DLTS, Photoluminescence (PL) and Micro-Raman techniques to investigate the effect of the orientation of the substrates on the structural, electrically and optically active defects in dilute GaAs1−xBix epilayers structures having a Bi composition x = ~5.4%, grown by Molecular Beam Epitaxy (MBE) on (100) and (311)B GaAs planes. X-ray diffraction results revealed that the in-plane strain in the Ga(As,Bi) layer of the samples grown on (100)-oriented substrate (−0.0484) is significantly larger than that of the samples grown on (311)

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B-oriented substrate. Paulauskas et al. [13] study scanning transmission electron microscopy techniques are employed to analyze the distribution of Bi in several distinctly MBE grown GaAs1−xBix alloys. Statistical quantification of atomic-resolution HAADF images, as well as numerical simulations, are employed to interpret the contrast from Bi-containing columns at atomically abrupt (001) GaAs-GaAsBi interface and the onset of CuPt-type ordering. Davidson et al. [14] investigate a novel class of strain-compensated type-II QWs combining electron-confining, tensile strained GaNyAs1−y and hole-confining, compressively strained GaAs1−xBix layers. They systematically analyses the opto-electronic properties of W-type GaAs1−x Bix/GaNyAs1−y QWs, and identify paths to optimize their threshold characteristics.

As natural extension to our previous work [7,8], a new calculation is performed by varying the composition of bismuth, we hope to throw light on the effect of additional Bi on the thermoelectric properties of $GaAs_{1-x}Bi_x$ alloys which are modeled using special quasi-random structures' (SQS) approach of Zunger et al. [11]. The $GaAs_{1-x}Bi_x$ alloys are promising materials for thermoelectric due to the expected decrease in thermal conductivity because of alloying with bismuth (as bismuth is a heavy atom and hence better gives phonon scattering).

2. Method of calculation

We have used 'special quasi-random structures' (SQS) approach of Zunger et al. [11] to reproduce the randomness of the $GaAs_{1-x}Bi_x$ alloys for the first few shells around a given site (see Fig. 1). This approach is

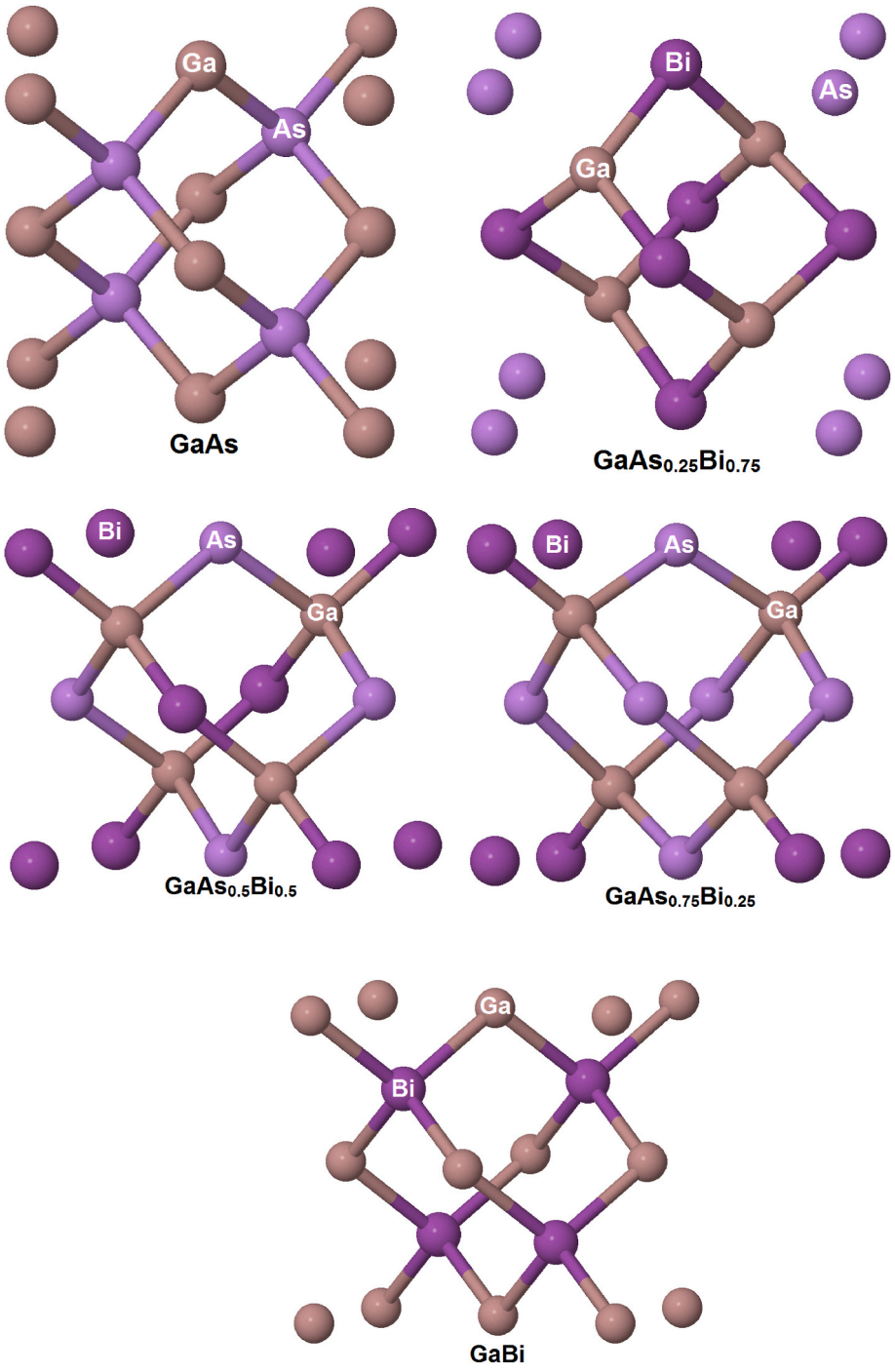

Fig. 1. The binary and ternary $GaAs_{1-x}Bi_x$ alloys are modeled using special quasi-random structures' (SQS) Zunger approach.

reasonably accurate to describe the physical properties that are not affected by the errors introduced by using the concept of periodicity beyond the first few shells [11]. For more details, we refer the reader to Ref. 7,8,11.

The total energy calculations were performed using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in Wien2k code [15]. The exchange correlation potential was treated using a modified Becke-Johnson potential (mBJ), which allows the calculation of band gaps with accuracy similar to the very expensive GW calculations [16]. It is a local approximation to an atomic "exact-exchange" potential and a screening term.

Thermoelectric properties of $GaAs_{1-x}Bi_x$ alloys are explored employing BoltzTraP code [17] which solves semiclassical Boltzmann transport equation within rigid band approximation and constant relaxation time (τ) approach [17]. Recently, BoltzTraP has been reasonably successful in calculating transport properties of next generation materials [18–21]. For a specific temperature (T) and chemical potential (μ), important parameters of electronic transport like electrical conductivity (σ), Seebeck coefficient (S), and electronic part of thermal conductivity (k_e) are calculated using the following relations, which are based on Fermi-dirac distribution function f_μ and energy dependent conductivity tensor $\overline{\sigma}_{\alpha\beta}(\varepsilon)$:

$$\sigma_{\alpha\beta}(T,\mu) = \frac{1}{\Omega}\int \overline{\sigma}_{\alpha\beta}(\varepsilon)\left[-\frac{\partial f_\mu(T,\mu)}{\partial \varepsilon}\right]d\varepsilon \quad (1)$$

$$S_{\alpha\beta}(T,\mu) = \frac{1}{eT\sigma_{\alpha\beta}(T,\mu)}\int \overline{\sigma}_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)\left[-\frac{\partial f_\mu(T,\mu)}{\partial \varepsilon}\right]d\varepsilon \quad (2)$$

$$\kappa^e_{\alpha\beta}(T,\mu) = \frac{1}{\Omega e^2 T}\int \overline{\sigma}_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)^2\left[-\frac{\partial f_\mu(T,\mu)}{\partial \varepsilon}\right]d\varepsilon \quad (3)$$

where α, β represents tensor indices, Ω and e dictates corresponding volume of the unit cell and electronic charge, respectively.

We have optimized the atomic positions of $GaAs_{1-x}Bi_x$ ternary alloys (structural relaxation), by minimization of the forces (1 mRy/au) acting on the atoms. Using the relaxed geometry various features including the transport properties can be calculated. Once the forces are minimized in this construction one can then find the self-consistent density at these positions by turning off the relaxations and driving the system to self-consistency.

The spherical harmonics inside non-overlapping muffin-tin (MT) spheres surrounding the atoms are expanded up to $l_{max} = 10$. The muffin-tin radii are 1.6 atomic units (a.u.) for Bi, whereas a 1.95 a.u. Is used for both Ga, and As. The plane wave cut-off of $K_{max} = 7.0/R_{MT}$ was chosen for the expansion of the wave-functions in the interstitial region for the binary compounds GaAs, GaBi and ternary alloys $GaAs_{1-x}Bi_x$. The charge density was Fourier expanded up to $G_{max} = 14$ (Ryd)$^{1/2}$. The irreducible wedge of the Brillouin zone (BZ) was described by a mesh of 35 special k-points for binary compounds and alloys, except for the case of x = 0.5, when a mesh of 64 special k-points is used. In the case of calculating the thermoelectric properties, we used denser meshes of 5000 k-points for binary as well as ternary alloys of $x = 0.25$ and 0.75, whereas 3000 k-points were used for $x = 0.5$. The self-consistent calculations are converged till the total energy of the system is stable within 10^{-5} Ry. The FP-LAPW + lo method has proven to be one of the accurate methods for computation of the electronic structure of solids within DFT [22–24].

3. Results and discussion

3.1. Salient features of the electronic band structures

Based on the calculated band structure, the semi-classical Boltzmann theory as implemented in the BoltzTraP code was used to study the influence of vary the Bi content on the thermoelectric properties of $GaAs_{1-x}Bi_x$ (x = 0, 0.25, 0.50, 0.75, 1.0) alloys as a function of temperature (T) at constant value of chemical potential (μ) with constant relaxation time (τ). Since the electronic band structure are the keynote factor for calculating the transport properties of the materials, thus let us recall the main features of the electronic band structure of $GaAs_{1-x}Bi_x$. The calculated electronic band structures of $GaAs_{1-x}Bi_x$ using mBJ are shown in Fig. 2a-d. The valence band maximum (VBM) and conduction band minimum (CBM) of $GaAs_{1-x}Bi_x$ alloys are situated at Γ point the center of the BZ resulting in a direct band gap of 1.42 eV, 0.449 eV, 0.052 eV, 0.016 eV and −0.0056 eV at x = 0.0, 0.25, 0.50, 0.75 and 1.0, respectively. These values along with the previous theoretical results and experimental data are presented in Table 1. It is clearly seen that the band gap values are close to the experimental data and confirm the variation of large energy gap bowing with concentration of Bi. The good agreement with experimental data reveals the accuracy of the selected exchange correlation potentials used here which confirm the accuracy of the theoretical calculations. It is clearly seen that the energy gap decreases with increasing Bi concentration. This reduction of the band gap is explained by the highly localized nature of the perturbation introduced by Bi atoms [25–30]. The largest contribution to the band gap reduction originates from structural relaxation and charge exchange that are, respectively, proportional to the differences in the atomic orbital size and energy of the As and Bi atoms [25,28]. Also the observed huge reduction in the energy band gap could be due to a resonant interaction between Bi *6p* state in the conduction band and the valence band maximum (VBM) [6–9].

3.2. Effective mass

The electronic band structures of $GaAs_{1-x}Bi_x$ alloys show that the bands are less dispersive for all high symmetry directions, suggesting that these alloys possess large effective mass for the carriers and hence a high thermopower. For better thermoelectric properties, we need to have high mobility (for higher electrical conductivity (σ) with reasonable carrier concentrations), higher band masses (to obtain higher value of Seebeck coefficient (S)) and lower lattice thermal conductivities ($k = k_e + k_l$), which consist of the electronic and phonon contributions. However, carriers with large mobility is required for obtaining a higher σ. The thermoelectric power factor can be improved, if the effective mass is increased, that is due to the fact that the gain in S is larger than the decrease in the mobility [22]. To determine the transport properties, we need to know the effective charge-carrier mass, S and σ.

From Fig. 2a–e, we obtained the effective mass of electrons (m_e^*) for the binary and ternary $GaAs_{1-x}Bi_x$ alloys. Usually we estimated the value of m_e^* from the conduction band minimum curvature (CBM). The diagonal elements of the effective mass tensor, m_e, for the electrons in the conduction band are calculated following this expression ($\frac{1}{m_e^*} = \frac{\partial^2 E(k)}{\hbar^2 \partial k^2}$). The effective mass of electron is assessed by fitting the electronic band structure to a parabolic function (above mentioned equation). We have calculated the electron effective mass ratio (m_e^*/m_e), effective mass of the heavy holes (m_{hh}^*/m_e) and light holes (m_{lh}^*/m_e), around Γ point the center of the BZ for the binary and ternary $GaAs_{1-x}Bi_x$ alloys. These values are listed in Table 2.

3.3. Thermoelectric properties

In the recent days, thermoelectric (TE) applications from emerging materials paid much more attention to reduce dependencies over conventional energy sources [31,32]. TE devices utilize those special materials to exhibit direct conversion of energy between heat and electricity. Performance of a TE material towards device application can be characterized through several important parameters such as electrical conductivity (σ), Seebeck coefficient (S), power factor (σS^2) and finally by checking TE figure of merit (ZT). A material with ZT ≥ 1 can

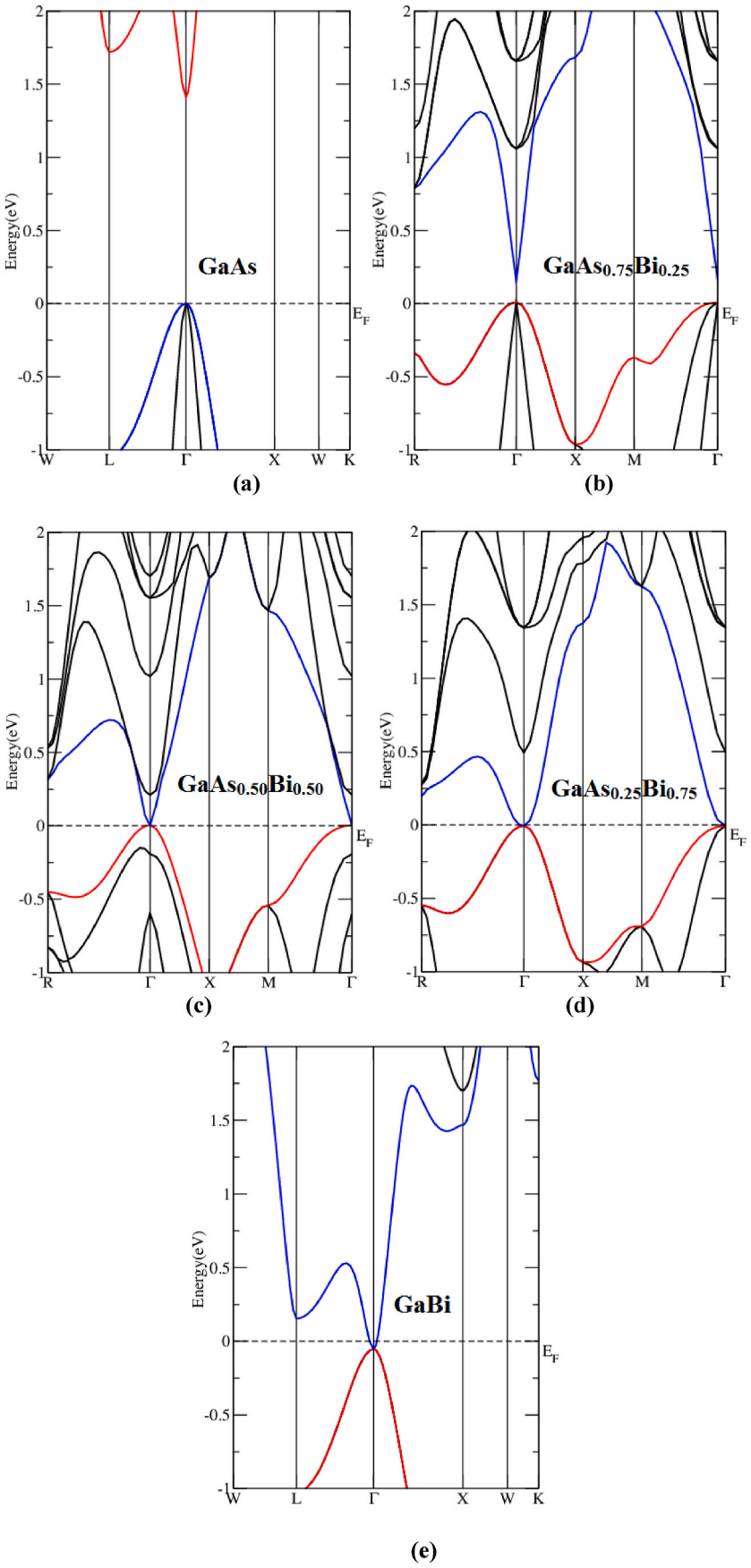

Fig. 2. The calculated electronic band structures for the binary and ternary $GaAs_{1-x}Bi_x$ alloys using mBJ approach.

Table 1
Band gap (eV) for $GaAs_{1-x}Bi_x$ (X = 0, 0.25, 0.50, 0.75, 1.0).

	Present work	theoretical work	Exp. Work
GaAs	1.41	1.2[a], 1.51[b], 1.52[c]	1.52[d]
$GaAs_{0.75}Bi_{0.25}$	0.449	0.38[a], 0.43[c]	
$GaAs_{0.50}Bi_{0.50}$	0.052	−0.32[a], −0.38[c]	
$GaAs_{0.25}Bi_{0.75}$	0.016	−0.98[a], −1.05[c]	
GaBi	−0.0056	−1.38[a], 1.45[b,c]	−1.45[d]

*Present work.
[a] [7].
[b] [48].
[c] [2].
[d] [49].

Table 2
Effective mass ration for $GaAs_{1-x}Bi_x$ (X = 0, 0.25, 0.50, 0.75, 1.0).

	GaAs	$GaAs_{0.75}Bi_{0.25}$	$GaAs_{0.50}Bi_{0.50}$	$GaAs_{0.25}Bi_{0.75}$	GaBi
m_e^*/m_e	0.0022	0.0042	0.0052	0.0071	0.0248
m_{hh}^*/m_e	0.0182	0.0145	0.0142	0.0157	0.0103
m_{lh}^*/m_e	0.0133	0.0022	0.0046	0.0055	0.0021

be regarded as a good TE material as well as suitable for device engineering [33]. In order to explore reliable TE variations, electronic band structure of the material is the key factor. In this study, electronic band structure using mBJ approximation has been utilized to explore TE variations. Previous study on GaAs and GaBi solar cells were studied in a high temperature range within 30–650C where their functionality and changes in surface topology were monitored [34–41]. That is why we have checked TE variations of $GaAs_{1-x}Bi_x$ (x = 0, 0.25, 0.50, 0.75, 1.0) alloys at room temperature as well as at some higher temperature regime. In this computations, electrical conductivity (σ) and electronic part of thermal conductivity (k_e) depends on τ whereas Seebeck response is independent of τ. Thus electrical conductivity (σ) and electronic part of thermal conductivity (k_e) are parametrized by τ as σ/τ and k_e/τ.

To calculate the electronic transport properties of the thermoelectric binary and ternary $GaAs_{1-x}Bi_x$ alloys between 0.0 and 1.0 with stepsize of 0.25, we used the semi-classical Boltzmann theory as incorporated in BoltzTraP code [17]. It is important to mention that in BoltzTraP code the relaxation time τ taken as a constant. The constant relaxation time approximation and the rigid band approximation were used in the calculations [17]. BoltzTrap code depends on a well-tested smoothed Fourier interpolation to obtain an analytical expression of bands. This is based on the fact that the electrons contributing to transport are in a narrow energy range due to the delta-function like Fermi broadening. For such a narrow energy range the relaxation time is nearly the same for the electrons. The accuracy of this method has been well tested earlier,

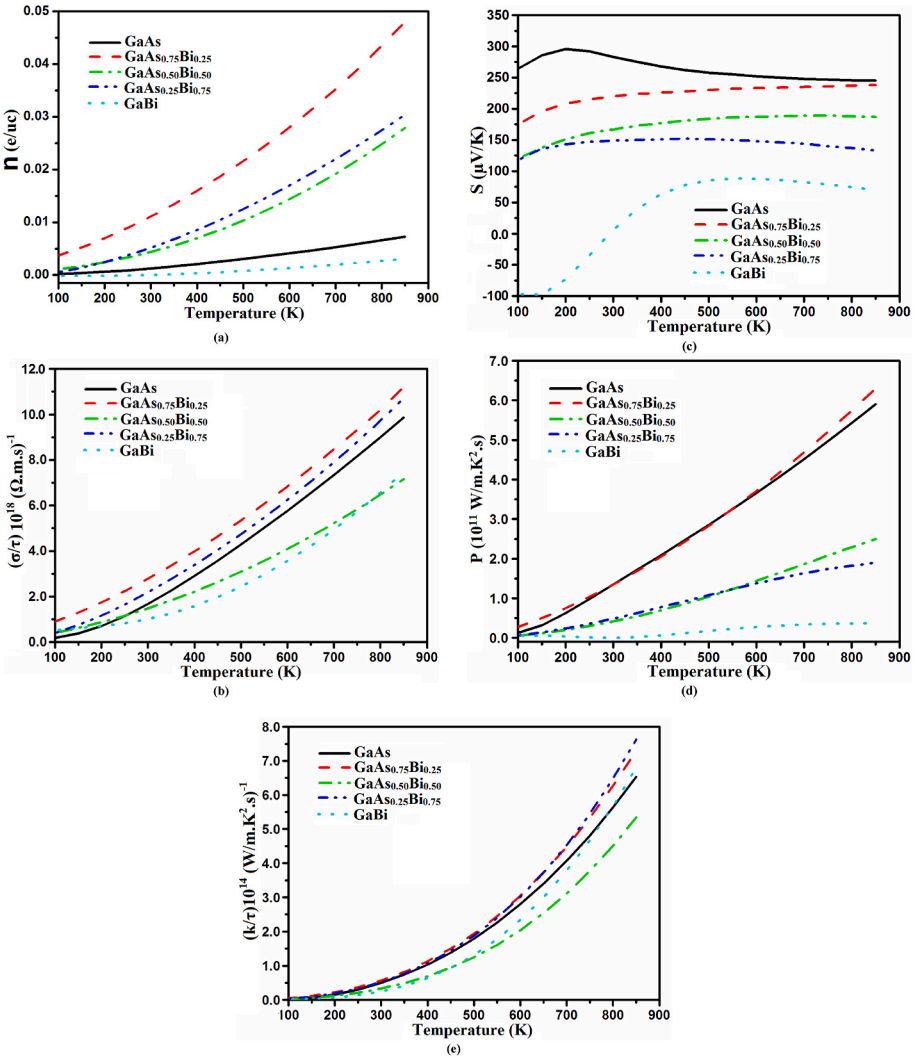

Fig. 3. Calculated electronic transport properties of the thermoelectric binary and ternary $GaAs_{1-x}Bi_x$ alloys, were obtained using the semi-classical Boltzmann theory as incorporated in BoltzTraP code; (a) The carrier concentration (n), (b) The electrical conductivity (σ/τ), (c) Seebeck coefficient (S), (d) The electronic power factor ($S^2\sigma/\tau$), (e) The electronic thermal conductivity (κ_e/τ). The transport properties are plotted as a function of temperature at certain value of chemical potential with constant relaxation time (τ). The calculated transport properties for the binary and ternary $GaAs_{1-x}Bi_x$ alloys are calculated using mBJ approach.

and the method actually turns out to be a good approximation [17, 42–45]. The BoltzTraP code has proven to be as a very efficient technique for calculating the electronic transport properties [23,24,46,47]. The carrier concentration (n), electrical conductivity (σ/τ), Seebeck coefficient (S), electronic thermal conductivity (k_e/τ) and the electronic power factor ($S^2\sigma/\tau$) as a function of T at constant value of chemical potential were calculated for the binary and ternary $GaAs_{1-x}Bi_x$ alloys between 0.0 and 1.0 with stepsize of 0.25.

Better thermoelectric properties are determined by a combination of high mobility and reasonable carrier concentration. In Fig. 3a we have illustrated the carrier concentration (n) of $GaAs_{1-x}Bi_x$ alloys as a function of temperature. One can see that n for the ternary alloys increases exponentially with increasing the temperature. As a remarkable finding we observe that the binary and the ternary alloys (x = 0.0, 0.5, 0.75 and 1.0) have zero n at 100 K, except $GaAs_{0.75}Bi_{0.25}$ possess 0.004 e/uc at 100 K. Also one can see the n for the parent's compounds exhibits insignificant increase in the carrier concentration with increasing the temperature, and both of them (parent's compounds) show the same tendency. This is attributed to the fact that, in the binary alloys, there are only two kind of atoms with certain electro-negativity differences. Thus for the binary alloys under investigation the electro-negativity difference between Ga and As atoms are similar as that between Ga and Bi, and, therefore the carrier concentrations in both alloys are similar. While, in the ternary alloys, there are three type of atoms with different concentrations, and, thus, the electro-negativity will be bigger between the atoms leading to more charge carrier concentrated around the atom which exhibit higher electro-negativity. This may could explain why $GaAs_{0.75}Bi_{0.25}$ exhibits the highest n among the others in the temperature range, and also why both of $GaAs_{0.5}Bi_{0.5}$ and $GaAs_{0.25}Bi_{0.75}$ show the same trends. The values of the carrier concentrations of $GaAs_{1-x}Bi_x$ alloys at 100 K and 850 K are presented in Table 3.

The electrical conductivity ($\sigma = ne\eta$) is related to the density of charge carriers (n) and their mobility ($\eta = e\tau/m_e$). The electrical conductivity (σ/τ) as a function of temperature between 100 and 850 K at a certain value of chemical potential was calculated and illustrated in Fig. 3b. The electrical conductivity for $GaAs_{1-x}Bi_x$ alloys increases exponentially with increasing the temperature. The rapid increase in the electrical conductivity with temperature is due to enhancing the charge carrier concentration and the mobility of the carriers in the conduction band of the binary and ternary alloys with increasing the temperature. Following Fig. 3b, one can see that the curve of σ/τ for GaAs is situated between that of x = 0.25 and 0.75 from up and x = 0.5 and 1.0 from down. That means when we substitute 0.25 of As atom by Bi, the alloy $GaAs_{0.75}Bi_{0.25}$ show the highest value of σ/τ at low and high temperature, suggesting that this increase is due to higher concentration of the free charge carriers. When we substitute half of As atoms by Bi ($GaAs_{0.5}Bi_{0.5}$) we notice that σ/τ drops below the values of GaAs and show low σ/τ at 800 K. Increasing the content of Bi to be three times than As ($GaAs_{0.25}Bi_{0.75}$) causes to increase σ/τ with increasing the temperature. Finally, with substituting all As atoms by Bi (GaBi), leads to a drop σ/τ to show the lowest values among the alloys. We should mention here the fluctuation in the values of σ/τ with changing the content of Bi atoms is attributed to the mobility and the concentration of the charge carrier. The size of Bi atom is much bigger than that of As atom, therefore, when we substitute As by Bi a compressive strain develops in the crystal [3–5], resulting in a significant modification in the electronic structure and hence in the thermoelectric properties of the pristine alloys. In Table 3 we have listed all values of σ/τ for $GaAs_{1-x}Bi_x$ alloys at 100 K and 850 K.

Fig. 3c, show the Seebeck coefficients (thermopower) of $GaAs_{1-x}Bi_x$ alloys as a function of temperatures. The thermopower is used to determine the majority carrier type. The Seebeck coefficient has an inverse relationship with electrical conductivity. At low temperature the Seebeck coefficient of GaAs increases with increasing the temperature to reach the maximum value at 200 K then decrees with increasing the temperature. Substituting quarter numbers of As atoms by Bi ($GaAs_{0.75}Bi_{0.25}$) causes to reduce S with respect to that of GaAs. From Fig. 3c it is clear that S for $GaAs_{0.75}Bi_{0.25}$ increases with temperature to reach a maximum at 850 K which is close to S value of GaAs at 850 K. With increasing Bi content to be equal to As content ($GaAs_{0.5}Bi_{0.5}$) the S values reduces in comparison $GaAs_{0.75}Bi_{0.25}$ in the whole temperature range. Further increase in Bi content ($GaAs_{0.25}Bi_{0.75}$) causes a further reduction in S values with increasing the temperature. Replacing all the As atoms by Bi in GaBi, causes dramatic chances in the S values, at low temperature (100–300) K, GaBi shows negative S which increases with increasing the temperature, that represents the n-type concentration. Above 300 K the S value cross the zero to positive values (p-try concentration) to reach the maximum value at 550 K then gradually reduces with increasing temperature. Fig. 3c suggest that $GaAs_{1-x}Bi_x$ (x = 0.0, 0.25, 0.5, 0.75) alloys represents the p-type carrier except GaBi represent n-type at low temperate till 300 K then above this temperature it represents the p-type carrier. In general increasing the temperature causes to enhance the hole doping in $GaAs_{1-x}Bi_x$ (x = 0.0, 0.25, 0.5, 0.75) alloys more than that in GaBi. Since bismuth metal has a negative thermopower near −55 μV/K, a connected network of metal clusters cannot be the cause of the conductivity or thermopower [48,49]. We have listed the values of S for $GaAs_{1-x}Bi_x$ alloys in Table 3.

The electronic power factor ($S^2\sigma/\tau$) is a keynote quantity for measuring transport properties. Following Fig. 3d, one can see that the power factor rapidly increases with increasing the temperature. It is clear that $GaAs_{0.75}Bi_{0.25}$ alloys show the highest power factor among the others. The low Bi content is optimal in improving σ/τ, and $S^2\sigma/\tau$, that is attributed to the surfactant effects of Bi. We find a huge reduction in $S^2\sigma/\tau$ with increasing Bi content, which is expected due of alloy scattering. GaBi shows the lowest electronic power factor. In general, we expect that increasing the temperature should yield a high power factor. We report $S^2\sigma/\tau$ values for $GaAs_{1-x}Bi_x$ alloys in Table 3.

Fig. 3e, represents the electronic thermal conductivity (k_e/τ) of $GaAs_{1-x}Bi_x$ alloys as function of temperature. Usually the thermal conductivity consists of two parts, electronic part (k_e) in which the electrons and holes are responsible for transporting heat and the phonon part (k_l)

Table 3
Thermoelectric properties for $GaAs_{1-x}Bi_x$ (x = 0, 0.25, 0.50, 0.75, 1.0).

Thermoelectric properties	100 K	850 K
Electrical conductivity		
GaAs	0.20×10^{18}	9.5×10^{18}
$GaAs_{0.75}Bi_{0.25}$	0.95×10^{18}	11.1×10^{18}
$GaAs_{0.5}Bi_{0.5}$	0.42×10^{18}	7.2×10^{18}
$GaAs_{0.25}Bi_{0.75}$	0.42×10^{18}	10.6×10^{18}
GaBi	0.52×10^{18}	7.3×10^{18}
Carrier Concentration		
GaAs	0.0002	0.0073
$GaAs_{0.75}Bi_{0.25}$	0.0037	0.0480
$GaAs_{0.5}Bi_{0.5}$	0.0011	0.0279
$GaAs_{0.25}Bi_{0.75}$	0.0005	0.0304
GaBi	−0.0002	0.0031
Seebeck coefficient		
GaAs	265	247
$GaAs_{0.75}Bi_{0.25}$	175	237
$GaAs_{0.5}Bi_{0.5}$	121	187
$GaAs_{0.25}Bi_{0.75}$	117	135
GaBi	−98.0	70
Thermal conductivity		
GaAs	0.04×10^{14}	6.54×10^{14}
$GaAs_{0.75}Bi_{0.25}$	0.05×10^{14}	7.05×10^{14}
$GaAs_{0.5}Bi_{0.5}$	0.04×10^{14}	5.38×10^{14}
$GaAs_{0.25}Bi_{0.75}$	0.05×10^{14}	7.52×10^{14}
GaBi	0.04×10^{14}	6.60×10^{14}
Power Factor		
GaAs	0.20×10^{11}	5.90×10^{11}
$GaAs_{0.75}Bi_{0.25}$	0.30×10^{11}	6.25×10^{11}
$GaAs_{0.5}Bi_{0.5}$	0.09×10^{11}	2.50×10^{11}
$GaAs_{0.25}Bi_{0.75}$	0.09×10^{11}	1.92×10^{11}
GaBi	0.09×10^{11}	0.36×10^{11}

where the phonons traveling through the lattice. We should emphasize that BoltzTraP code calculates only the electronic part i.e only k_e. The k_e/τ can be estimated from the electrical conductivity $\sigma/\ \tau$ using the Wiedemann-Franz law. The electronic thermal conductivity increases exponentially with increasing the temperature. The parent GaAs exhibits a rapid increase in k_e/τ with the temperature. Substituting 1/4 of As atoms by Bi ($GaAs_{0.75}Bi_{0.25}$) the electronic thermal conductivity increases above the values of GaAs. Further increasing of Bi content to be the numbers of As atoms equal to that of Bi atoms ($GaAs_{0.5}Bi_{0.5}$) led to reduce k_e/τ to exhibit the lower values in the whole temperature range. More Bi content ($GaAs_{0.25}Bi_{0.75}$) causes to increase $k_e/\ \tau$ to be similar to that of ($GaAs_{0.75}Bi_{0.25}$). Finally substituting all As atoms by Bi atoms (GaBi) leads to reduce k_e/τ to lower than that of GaAs.

For thermoelectric power generation (TPG), the efficiency is calculated using $ZT = S^2\sigma T/\kappa$. Large ZT leads to better efficiency, but increasing ZT in bulk semiconductors ($ZT \leq 1$) has proven to be difficult because of the variables' interdependence; a reduction in $k_e/\ \tau$ typically leads to a reduction in σ/τ. Similarly, S has an inverse relationship with σ/τ. In the absence of any calculations or measurements of the lattice thermal conductivity it is difficult to which alloy will have the largest figure of merit (FOM). We show that low Bi concentrations are optimal in improving the conductivity, Seebeck coefficient, and thermoelectric power factor, possibly due to the surfactant effects of bismuth. We observed a reduction in thermal conductivity with increasing Bi concentration, which is expected because of alloy scattering [39].

4. Conclusions

The starting point of calculating the thermoelectric properties the $GaAs_{1-x}Bi_x$ alloys are modeled using special quasi-random structures' (SQS) Zunger approach. Using the calculated electronic band structures the electronic transport properties of the thermoelectric of the $GaAs_{1-x}Bi_x$ alloys, were obtained using the semi-classical Boltzmann theory as incorporated in BoltzTraP code. The carrier concentration (n), electrical conductivity (σ/τ), Seebeck coefficient (S), electronic thermal conductivity (k_e/τ) and the electronic power factor ($S^2\sigma/\ \tau$) as a function of temperature at certain value of chemical potential were calculated. Our calculations show that $GaAs_{0.75}Bi_{0.25}$ exhibits the higher carrier concentration and hence the higher electronic conductivity and power factor, while GaAs shows the highest value for Seebeck coefficient. GaBi exhibits the lowest values for the transport properties. Our work shows that $GaAs_{1-x}Bi_x$ alloys could be promising materials for thermoelectric applications due to the expected decrease in thermal conductivity arising from alloying with bismuth (being a heavy atom gives better phonon scattering).

Notes

The symbol (μ) refers to chemical potential and (η) to the mobility.

CRediT authorship contribution statement

A.H. Reshak: Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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