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Band gaps and charge distribution in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals

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Abstract. Pseudopotential investigation of energy band gaps and charge distribution in quasi-binary $(\mathrm{GaSb})_{1-x}(\mathrm{InAs})_x$ crystals has been reported. To the best of our knowledge, there had been no reported theoretical work on these materials. In agreement with experiment, the quasi-binary crystals of interest showed a significant narrowing of the optical band gap compared to the conventional $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{As}_y\mathrm{Sb}_{1-y}$ quaternary alloys (with $x = 1 - y$). Moreover, the absorption at the optical gaps indicated that $(\mathrm{GaSb})_{1-x}(\mathrm{InAs})_x$ is a direct Γ to Γ band-gap semiconductor within a whole range of the x composition. The information derived from the present study predicts that the band gaps cross very important technological spectral regions and could be useful for thermophotovoltaic applications.

PACS. 71.20.–b Electron density of states and band structure of crystalline solids – 71.23.Ft Quasicrystals – 71.28.+d Narrow-band systems

1 Introduction

III-V compound semiconductors are extensively studied, in particular, due to their applicability in optical and optoelectronic devices. These semiconductors crystallize in the zinc-blende structure which corresponds to the space group T_d and have a tetrahedrally oriented binding between period-III and period-V elements mediated by eight electrons per basis from the upper-most s and p shells [1,2]. Binary compound semiconductors maintain a limited number of discrete properties (band gap and lattice constant), whereas numerous applications require intermediate properties (between those of binary compounds) [3]. The desired intermediate properties can be obtained through ternary alloys [3,5]. In practice, the growth of bulk ternary alloys is a formidable task, due to the wide separation between the solidus-liquidus curves of the pseudo-binary phase diagram which arises mainly from the lattice mismatch and the melting points of the parent compounds forming the alloy of interest [5–7]. Lattice matching to a binary compound can be achieved by forming quaternary alloys. This can add an additional degree of freedom for band gap and lattice parameter tuning. However, miscibility gaps in the pseudo-quaternary systems and phase separation are the main obstacles for quaternary alloy solidification from melts [6,8,9]. These arise mainly from differences in chemical interaction between the constituent elements in the melt [6].

Recently, a new class of III-V quasi-binary $[\mathrm{A_{III}B}_V]_{1-x}[\mathrm{C_{III}D}_V]_x$ semiconductor alloys has been synthesized and bulk crystals grown from the melt for the first time by Dutta and Ostrogorsky [5,6]. The investigation was focused on $(\mathrm{GaSb})_{1-x}(\mathrm{InAs})_x$ $(0 < x < 0.05)$ due to its importance for thermo-photovoltaic applications. These experimental studies have demonstrated that the quasi-binary semiconductor alloys possess better crystalline perfection (crack free and are single phase) and compositional homogeneity (close to unity segregation) than melt grown bulk ternary and quaternary alloys.

In addition to these experimental advances, reliable computational methods for electronic structure may provide important complementary data to the experimental work, determining the energy band gap that is known to be one of the most important device parameters since it is strongly connected with the operating wavelength of the optoelectronic devices, and predicting the electronic charge distribution which yields useful information about the bonding properties.

In order to give some complementary theoretical data to the experimental works cited above regarding $(\mathrm{GaSb})_{1-x}(\mathrm{InAs})_x$, we have carried out theoretical calculations of energy band gaps and electronic charge distribution for quasi-binary $(\mathrm{GaSb})_{1-x}(\mathrm{InAs})_x$ crystals using the pseudopotential formalism under the virtual crystal approximation. To make allowance for the compositional disorder, a correction to the alloy potential has been introduced. To the best of our knowledge, this is the first time a theoretical study has been carried out on such a quasi-binary crystals. The motivation of

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the present work is that GaSb-InAs quasi-binary systems have close lattice constants and were found experimentally to exhibit band gaps and structural quality [5] significantly different from that of a conventional quaternary alloy $Ga_{1-x}In_xAs_{1-y}Sb_y$ with $x = y$.

The article is organized as follows. In Section 1, we give a brief introduction, followed by the description of the method used in the calculations in Section 2. The results are presented and discussed in Section 3. A summary is given in Section 4.

2 Computational method

In carrying out the empirical pseudopotential calculations, we have essentially used the local pseudopotential method. The pseudopotential Hamiltonian,

$$H = -\left(\frac{\eta^2}{2m}\right)\nabla^2 + V(r) \tag{1}$$

contains an effective potential which is expanded as Fourier series in reciprocal lattice space.

For the case of N-(8-N) compounds with a zinc-blende structure, the structure and form factors are expressed as follows,

$$S^{\mathrm{S}}(G) = \cos G\tau, \qquad S^{\mathrm{A}}(G) = \sin G\tau \tag{2}$$

$$V_G^{\mathrm{S}} = \frac{1}{2}[V_1(G) + V_2(G)] \tag{3a}$$

$$V_G^{\mathrm{A}} = \frac{1}{2}[V_1(G) - V_2(G)] \tag{3b}$$

Here, $\tau = (a/8)(1,1,1)$, half the vector between the two atoms contained in the unit cell, a being the lattice constant, and $V_1(G)$ and $V_2(G)$ are the pseudopotential form factors of the individual atoms in the unit cell. The pseudopotential form factors are determined empirically by fitting the calculated band structure of parent compounds to experimental data. Good agreement with known band energies was required at the chosen symmetry points in the Brillouin zone. For the materials GaSb and InAs being studied here, the experimental band gap energies used in the fitting procedure were taken from references [10–12], and given in Table 1, alongside with our obtained calculated ones. The empirical pseudopotential parameters are determined by using the non-linear least-squares method in which all of the parameters are simultaneously optimized under a definite criterion of minimizing the root-mean-square deviation [13]. The dimension of our eigenvalue problem is a (136×136) matrix. However, 59 plane waves give a good convergence.

For the quasi-binary $(\mathrm{GaSb})_{1-x}(\mathrm{InAs})_x$ crystals under investigation, the symmetric and antisymmetric form factors are obtained as [14],

$$V_G^{\mathrm{S,A}} = (1-x)V_{\mathrm{GaSb}}^{\mathrm{S,A}} + xV_{\mathrm{InAs}}^{\mathrm{S,A}} - p[x(1-x)]^{\frac{1}{2}}\left(V_{\mathrm{InAs}}^{\mathrm{S,A}} - V_{\mathrm{GaSb}}^{\mathrm{S,A}}\right) \tag{4}$$

Table 1. Band-gap energies of GaSb and InAs.

Compound	Band-gap energy (eV)		
	E_g^{Γ}	E_g^{X}	E_g^{L}
GaSb	0.725 [10,11]	1.03 [11]	0.761 [11]
	0.72[a]	1.02[a]	0.78[a]
InAs	0.36 [12]	1.37 [12]	1.07 [12]
	0.36[a]	1.37[a]	1.07[a]

[a] Present calculations.

where p is an adjustable parameter simulating the disorder effect. Thus, $p = 0$ when the virtual crystal approximation is used alone and has a value of -2.32 when the compositional disorder is taken into consideration.

The lattice constant of the quasi-binary crystal of interest is calculated using the Vegard's law [15],

$$a(x) = (1-x)a_{\mathrm{GaSb}} + xa_{\mathrm{InAs}} \tag{5}$$

The electronic wave functions were obtained from the band-structure calculation. These wave functions are then used to compute the charge density by noting that the probability of finding an electron in a certain spatial region of volume $\mathrm{d}\Omega$ is given by $|\Psi_{n,k}(r)|^2\mathrm{d}\Omega$, where n is the index of the energy eigenvalue associated with the state k.

The charge density for each valence band may be written as,

$$\rho_n(r) = \sum_k e|\Psi_{n,k}(r)|^2 \tag{6}$$

where the summation is over all states in the Brillouin zone for a given band n.

The total charge density for a semiconductor can be obtained by adding the charge density from all the valence bands, that is,

$$\rho(r) = \sum_n \rho_n \tag{7}$$

where the sum is over all occupied bands.

In our case, we were interested only in the total valence charge density at the high symmetry point Γ in the Brillouin zone for specific band, thus,

$$\rho(r) = e|\Psi_{n,k}(r)|^2 \tag{8}$$

3 Results

In Table 2, we give our final local adjusted symmetric V_{S} and antisymmetric V_{A} pseudopotential form factors as well as used lattice constants for GaSb and InAs.

In Figure 1, we show the variation of the fundamental band gap energy E_g^{Γ} as a function of composition x for $(\mathrm{GaSb})_{1-x}(\mathrm{InAs})_x$ quasi-binary crystals. In view of this figure, one can note that the neglect of compositional disorder, *i.e.* the use of the VCA alone, leads to an almost linear decrease of E_g^{Γ} with increasing x showing a very weak band gap bowing parameter of -0.04 eV (Fig. 1, solid line). This value does not appear to be in quantitative

Table 2. Pseudopotential form factors and lattice constants for GaSb and InAs.

Compound	Form factors (Ry)						Lattice constant (Å)
	$V_S(3)$	$V_S(8)$	$V_S(11)$	$V_A(3)$	$V_A(4)$	$V_A(11)$	
GaSb	-0.191206	0.005	0.043533	0.045340	0.03	0.00	6.118
InAs	-0.217669	0.011	0.041633	0.054731	0.039485	0.024	6.058

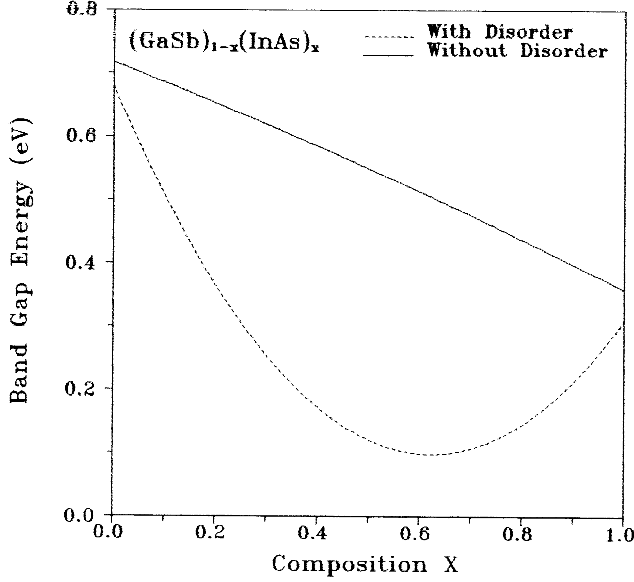

Fig. 1. Direct band-gap energy (E_g^{Γ}) in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals as a function of composition x.

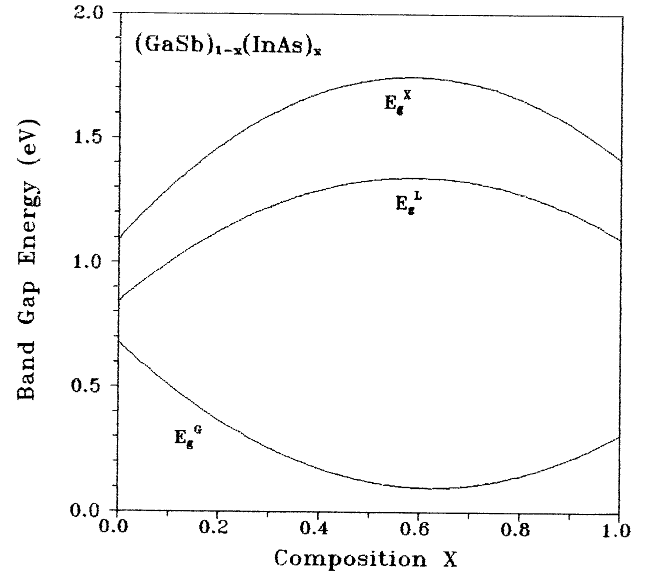

Fig. 2. Direct (E_g^{Γ}) and indirect (E_g^{X} *and* E_g^{L}) band gap energies in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals as a function of composition x.

agreement with the experimental one of 1.5 eV recently reported by Dutta and Ostrogorsky [6]. This is not the case when the compositional disorder is taken into account (Fig. 1, dashed line). The E_g^{Γ} in that case decreases non-linearly exhibiting a strong band-gap bowing parameter of 1.50 eV. This value is reached for $p = -2.32$. This provide a support to the fact that the band-gap bowing parameter is less important when the compositional disorder is ignored usually reported for narrow-gap mixed III-V ternary alloys [16,17]. It should be noted also that the value of the band-gap bowing parameter of $(GaSb)_{1-x}(InAs)_x$ is generally much higher than those reported for ternary semiconductor alloys [12,18] showing the more important effect of the compositional disorder on quasi-binary crystals as compared to that on ternary alloys. According to Dutta and Ostrogorsky [6] such a large bowing in the quasi-binary is probably due to alterations in the local bond structures between the Ga-Sb and In-As.

By including the disorder effect, we have calculated the variation of the direct (E_g^{Γ}) and indirect (E_g^{X}) and (E_g^{L}) energy band-gaps *versus* composition x for quasi-binary crystals of interest. Our results are plotted in Figure 2. Unlike the decrease of the direct band gap (E_g^{Γ}), an increase of both indirect band-gaps E_g^{X} and E_g^{L} with increasing x from 0 to 1 can be clearly seen. The curves of Figure 2 represent a fit by a least-squares procedure according to the analytical expressions,

$$E_g^{\Gamma}(\text{eV}) = 0.68 - 1.86x + 1.50x^2 \tag{9}$$

$$E_g^{X}(\text{eV}) = 1.09 + 2.24x - 1.91x^2 \tag{10}$$

$$E_g^{L}(\text{eV}) = 0.84 + 1.69x - 1.44x^2. \tag{11}$$

The quadratic terms in equations (9–11) are referred to as band-gap bowing parameters. All these bowing parameters are large in magnitude indicating that the E_g^{Γ}, E_g^{X}, E_g^{L} band-gap energies are sensitive to the alloying disorder effect. Interestingly as well, one can note that the absorption at the fundamental optical gaps in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals is predicted to be direct ($\Gamma \to \Gamma$) within a whole range of the x composition ($0 \le x \le 1$) since E_g^{Γ} is much lower than E_g^{X} *and* E_g^{L}, especially for larger values of x.

The experimental work by Dutta and Ostrogorsky [6] on quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals grown from melt showed that the family of the latter are different from the conventional $Ga_{1-x}In_xAs_ySb_{1-y}$ quaternaries due to growth behavior and physical properties. Such a result has

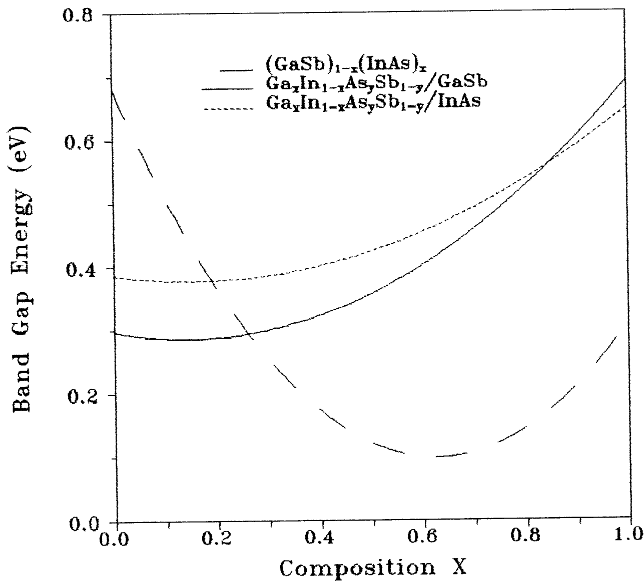

Fig. 3. Direct band gap energy (E_g^Γ) in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals and $Ga_xIn_{1-x}As_ySb_{1-y}$/GaSb and $Ga_xIn_{1-x}As_ySb_{1-y}$/InAs quaternary alloys as a function of composition x.

motivated us to compare between the behavior of E_g^Γ with composition x in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals and quaternary alloys $Ga_xIn_{1-x}As_ySb_{1-y}$/GaSb and $Ga_xIn_{1-x}As_ySb_{1-y}$/InAs using the same scheme in the calculation of quaternary alloys properties as that used in our previous publications [19,20] where effects of compositional variations are included. The lattice matching conditions for $Ga_xIn_{1-x}As_ySb_{1-y}$ quaternary system on GaSb and InAs substrates were as follows:

For GaSb substrate:

$$y = \frac{0.372 - 0.372x}{0.432 + 0.033x} \cdot \qquad (0 \le x \le 1) \qquad (12a)$$

For InAs substrate:

$$y = \frac{0.432 - 0.372x}{0.432 + 0.033x} \cdot \qquad (0 \le x \le 1) \qquad (12b)$$

Our results are depicted in Figure 3. It is clearly evident from this figure that the present data (E_g^Γ) of quasi-binary deviates from that expected in quaternary alloys $Ga_xIn_{1-x}As_ySb_{1-y}$/GaSb and $Ga_xIn_{1-x}As_ySb_{1-y}$/InAs showing band gaps significantly lower than the quaternaries for larger values of x. Interestingly as well, a strong band gap narrowing in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals could be noted as compared to quaternary alloys $Ga_{1-x}In_xAs_ySb_{1-y}$ (with $x = 1 - y$) as shown in Table 3. This behavior agrees very well with the experimental results reported in references [5,6]. According to [6], the possible origins of the band gap narrowing include chemical and structural alterations in the grown crystals, resulting from the association of Ga-Sb and In-As in the melt. This band-gap narrowing for quasi-binary crystals of interest has several technological applications. For example,

Table 3. Band gap energy (E_g^Γ) of $Ga_xIn_{1-x}As_ySb_{1-y}$ (with $x = 1 - y$) and $(GaSb)_{1-x}(InAs)_x$ at different compositions x.

Material	Band-gap energy (eV)
$Ga_{0.50}In_{0.50}As_{0.50}Sb_{0.50}$	0.395
$(GaSb)_{0.50}(InAs)_{0.50}$	0.150
$Ga_{0.40}In_{0.60}As_{0.60}Sb_{0.40}$	0.390
$(GaSb)_{0.40}(InAs)_{0.60}$	0.121
$Ga_{0.30}In_{0.70}As_{0.70}Sb_{0.30}$	0.389
$(GaSb)_{0.30}(InAs)_{0.70}$	0.108
$Ga_{0.20}In_{0.80}As_{0.80}Sb_{0.20}$	0.387
$(GaSb)_{0.20}(InAs)_{0.80}$	0.115

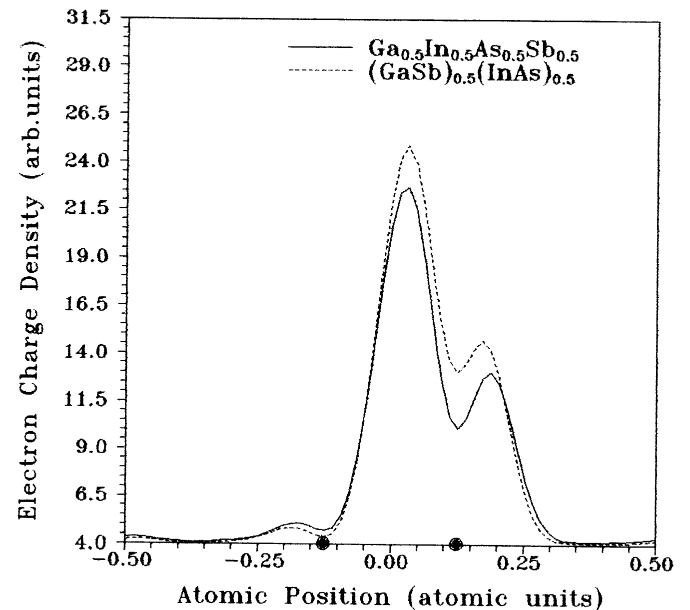

Fig. 4. Total valence charge density along the [111] direction at the Γ point for quasi-binary $(GaSb)_{0.50}(InAs)_{0.50}$ crystal and $Ga_{0.50}In_{0.50}As_{0.50}Sb_{0.50}$ quaternary alloy.

in the range 0.45–0.60 eV, the applications involve low cost thermophotovoltaic generation of electricity. Also dilute alloys of quasi-binary can give the same band gap as the concentrated alloys of ternary leading to improvement in structural properties of the crystals which improve the performances of devices fabricated on them [6].

It might be useful as well to compute the charge distribution for the quasi-binary crystals under investigation that may give an idea about the bonding properties. For that purpose, the computed total valence electron charge density along the [111] direction at the Γ point for quasi-binary $(GaSb)_{0.50}(InAs)_{0.50}$ crystal is displayed in Figure 4 (dashed line). Accordingly, most of the electronic charge density is shifted towards the anion and localized in the bonding region, whereas no significant charge in the interstitial regions could be seen (ionic bonding). This picture is generally common for III-V multicomponent alloys [20–22]. In order to compare between the charge

distribution of $(GaSb)_{0.50}(InAs)_{0.50}$ and that of the quaternary alloy $Ga_{0.50}In_{0.50}As_{0.50}Sb_{0.50}$, the charge density of the latter was also shown in Figure 4 (solid line). We can state that the shape of the profile does not completely changed. The maximum value of the charge distribution of valence electrons that gives the main contribution to the formation of chemical bond is decreased with respect to that of $(GaSb)_{0.50}(InAs)_{0.50}$. A downward shift of the charge distribution at the anion site and towards the cation in the bonding region is clearly seen, accompanied by a slight upward shift at the cation site. All these facts leads us to believe that the ionic character of quasi-binary $(GaSb)_{0.50}(InAs)_{0.50}$ crystals is stronger than that of $Ga_{0.50}In_{0.50}As_{0.50}Sb_{0.50}$ quaternary alloy.

4 Conclusion

Energy band gaps and charge distribution in quasi-binary $(GaSb)_{1-x}(InAs)_x$ crystals are investigated using the empirical pseudopotential method under the virtual crystal approximation to which the compositional disorder effect is added as an effective potential. A summary of the key findings follows: (i). The contribution of the compositional disorder is very important and must be included in the energy band-gap calculations to get meaningful agreement with the experiment. (ii). The absorption at the fundamental optical gaps showed that $(GaSb)_{1-x}(InAs)_x$ is a direct band-gap semiconductor within a whole range of the x composition. (iii). In agreement with experiment, significant optical band gap narrowing was found in quasi-binary crystals of interest as compared to conventional quaternary alloys (Ga-In-As-Sb) which leads to improvement in structural properties of the crystals and hence would improve the performances of devices fabricated on them. (iv). The electronic charge distributions indicated that the ionic character becomes stronger when passing from $Ga_{0.50}In_{0.50}As_{0.50}Sb_{0.50}$ quaternary alloy to quasi-binary $(GaSb)_{0.50}(InAs)_{0.50}$ crystal.

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