Valence Band Anticrossing in $GaBi_xAs_{1-x}$

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ABSTRACT

The optical properties of $GaBi_xAs_{1-x}$ ($0.04 < x < 0.08$) grown by molecular beam epitaxy have been studied by photomodulated reflectance spectroscopy. The alloys exhibit a strong reduction in the bandgap as well as an increase in the spin-orbit splitting energy with increasing Bi concentration. These observations are explained by a valence band anticrossing model, which shows that a restructuring of the valence band occurs as the result of an anticrossing interaction between the extended states of the GaAs valence band and the resonant T_2 states of the Bi atoms.

The incorporation of dilute concentrations of Bi into GaAs to produce $GaBi_xAs_{1-x}$ has been shown to induce a strong reduction of the bandgap (~ 90 meV per $x = 0.01$) as well as enhance the spin-orbit splitting energy quite considerably [1-5]. The ability to tune both of these properties over a wide energy spectrum through careful control of the alloy composition makes $GaBi_xAs_{1-x}$ an attractive candidate for potential applications such as long wavelength emitters and detectors as well as spintronic-related devices [2,5]. However, in order to optimize the electronic structure of $GaBi_xAs_{1-x}$, a sound understanding of the fundamental origins of the shifts in the bandgap and spin-orbit splitting energies is required. While it has been suggested that a perturbation of the electronic structure by a Bi defect level resonant with the valence band of GaAs is responsible for this phenomenon [6], the exact physical mechanism by which this occurs is not well understood.

It has been shown previously that the optical properties of ternary alloys containing anion species that are highly mismatched in atomic radius, such as $GaAs_xN_{1-x}$, $ZnTe_xS_{1-x}$ and $ZnTe_xSe_{1-x}$, are described by a valence band anticrossing (VBAC) model [7,8]. This model predicts that the localized defect states introduced by the minority species of large atomic radii hybridize with the extended states of the host semiconductor and induce a restructuring of the valence band. Recently, the VBAC model has been extended to $GaBi_xAs_{1-x}$ to explain the band gap bowing that has been observed in this dilute alloy over a narrow range of Bi concentrations [9]. Because this model treats the entire valence band, the shift in the spin-orbit splitting energy may also be explained within the context of these anticrossing interactions.

In this letter we present our investigation of the optical properties of $GaBi_xAs_{1-x}$ containing large Bi concentrations up to $x = 0.084$. Photomodulated reflectance spectroscopy (PR) indicates that both the band gap and spin-orbit splitting energies exhibit significant bowing away from the linearly interpolated trends between those values of the endpoint compounds. We show that these results are consistent with the VBAC model, which predicts a non-linear shift of the valence band edge that affects both the bandgap and spin-orbit splitting energies.

When a large, metallic isovalent impurity is substituted onto the anion sublattice of a host semiconductor, it introduces T_2 symmetric localized defect states that interact with the extended states of the host. If the impurity species has a significantly lower electronegativity and ionization energy than the majority anion element, these defect levels are located near the valence band edge of the host semiconductor. Hybridization of the states results in a restructuring of the heavy-hole (HH), light-hole (LH) and spin-orbit split-off (SO) bands into a series of E_+ and E_- sub-bands, which are described by a 12 x 12 Hamilitonian matrix. Details of the model are presented in a previous report [9]. In the case of $GaBi_xAs_{1-x}$, Bi introduces four primary and two spin-orbit split-off *p*-like defect levels located approximately 0.4 eV and 2.6 eV below the valence band maximum (VBM) of GaAs, respectively [10]. Because GaBi has not yet been synthesized, we use a theoretically predicted band gap of -1.45 eV and spin-orbit splitting energy of 2.2 eV, as well as a linear extrapolation of the trend in band edge positions of the Ga-V series to determine the band offsets between GaAs and GaBi [6,9]. These assumptions predict a type II band alignment between GaAs and GaBi, with a valence band offset, ΔE_{VBM}, of 0.6 eV, a conduction band offset, ΔE_{CBM}, of -2.3 eV, and a spin-orbit split-off band offset,

ΔE_{SO}, of -1.3 eV. The coupling parameter, C_{Bi}, which is a measure of the strength of the interactions and is dependent on the difference in the ionization energy between As and Bi, is adjustable and is used to fit the model with the experimental results. The calculated dispersion relations of the valence band of $GaBi_{0.04}As_{0.96}$ are shown in Fig. 1 as an example of the valence band restructuring. Six spin degenerate sub-bands are formed as the result of the interaction, and depending on the origin of the interacting states, they can be grouped into pairs of E_+ and E_- sub-bands. While the E_+ bands maintain a significant amount of the extended nature of the host, the E_- sub-bands retain a considerable amount of localized character, as they originate from the Bi defect states.

In order to experimentally examine the restructuring of the valence band, we have measured the inter-band transition energies of several $GaBi_xAs_{1-x}$ samples with compositions of $0.044 < x < 0.084$ grown by molecular beam epitaxy on semi-insulating GaAs substrates [11]. The optical transitions were determined by PR at room temperature. The 325 nm line of a chopped HeCd laser provided the photomodulation, while the probe beam was comprised of quasi-monochromatic light from a 300 W halogen tungsten lamp dispersed through a 0.5 m monochromator. Both Si and Ge photodiodes were used to detect the PR signal, and the transition energies were determined by fitting the spectra to the Aspnes third-derivative functional form [12]. The thickness and composition of the $GaBi_xAs_{1-x}$ films and GaAs capping layers were verified with Rutherford backscattered spectrometry.

The PR spectra of the $GaBi_xAs_{1-x}$ samples, displayed in Figure 2, each exhibit four clearly defined transitions related to inter-band optical transitions at critical points in the band structure of both the GaAs capping layer and $GaBi_xAs_{1-x}$ film. The composition

independent transitions at 1.43 eV and 1.77 eV correspond to the band gap (E_g) and spin-orbit split-off band to conduction band edge ($E_g + \Delta_0$) transitions in the GaAs capping layer, respectively. The low energy transition corresponds to the fundamental band gap (E_g) of the $GaBi_xAs_{1-x}$ film, the composition dependence of which is consistent with previous reports [1-4]. Finally, the intermediate feature around 1.7 eV is associated with the transition from the spin-orbit split-off E_+ sub-band to conduction band edge ($E_g + \Delta_0^+$). The specific energies of each transition as well as the associated broadening parameters used to fit the transitions are displayed in Tab. 1.

The composition dependence of the experimentally determined inter-band transition energies of the $GaBi_xAs_{1-x}$ films is shown in Fig. 3a, along with the values reported in the literature for samples of lower Bi concentrations [1-5]. The optical transition energies predicted by the VBAC model corresponds quite well with the experimental results using a coupling parameter of $C_{Bi} = 1.6$ eV. Insight into the behavior of these transition energies can be gleaned from inspection of the VBAC-determined valence band edge alignments displayed in Fig. 3b. The strong anticrossing interaction between the heavy and light hole bands and the localized Bi state results in a large upward shift of the resulting *HH/LH* E_+ bands with increasing Bi concentration. The non-linear upward movement in energy of these band edges is the primary cause of the band gap bowing observed in $GaBi_xAs_{1-x}$. Likewise, there is also an interaction between the spin-orbit split-off band and the localized spin-orbit split-off states of the Bi atoms. However, the intensity of the interaction is weakened by the considerable separation between these sets of coupled states.

The composition dependence of the $GaBi_xAs_{1-x}$ bandgap and spin-orbit splitting energies is shown in Fig. 3c. Out to compositions of $x = 0.084$, the band gap of $GaBi_xAs_{1-x}$ exhibits significant bowing with an initial decrease of approximately 90 meV per $x = 0.01$. The reduced composition dependence of the $E_g + \Delta_0^+$ transition compared to that of the E_g transition also produces a bowing of the spin-orbit splitting energy (Δ_0^+), which increases by roughly 50 meV per $x = 0.01$. It is seen in Fig 1 that the anticrossing interaction modifies the valence band dispersion relations resulting in distinctly nonparaolic bands. The broadening of the heavy-hole E_+ band is expected to increase the hole effective mass and strongly influence the hole transport properties in $GaBi_xAs_{1-x}$ alloys.

In summary, the VBAC model provides a fundamental, physical explanation for the experimentally observed large reduction of the band gap and increase of the spin-orbit splitting energies in $GaBi_xAs_{1-x}$. Anticrossing interactions between the extended states of GaAs and the localized states of the Bi impurities leads to a restructuring of the valence band into E_+ and E_- sub-bands, which in turn causes the bowing in the bandgap and spin-orbit splitting energies.

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FIGURE CAPTIONS

Fig 1. Dispersion relation of the $GaBi_{0.04}As_{0.96}$ valence band, containing the heavy-hole (HH), light-hole (LH) and spin-orbit split-off (SO) E_+ and E_- sub-bands.

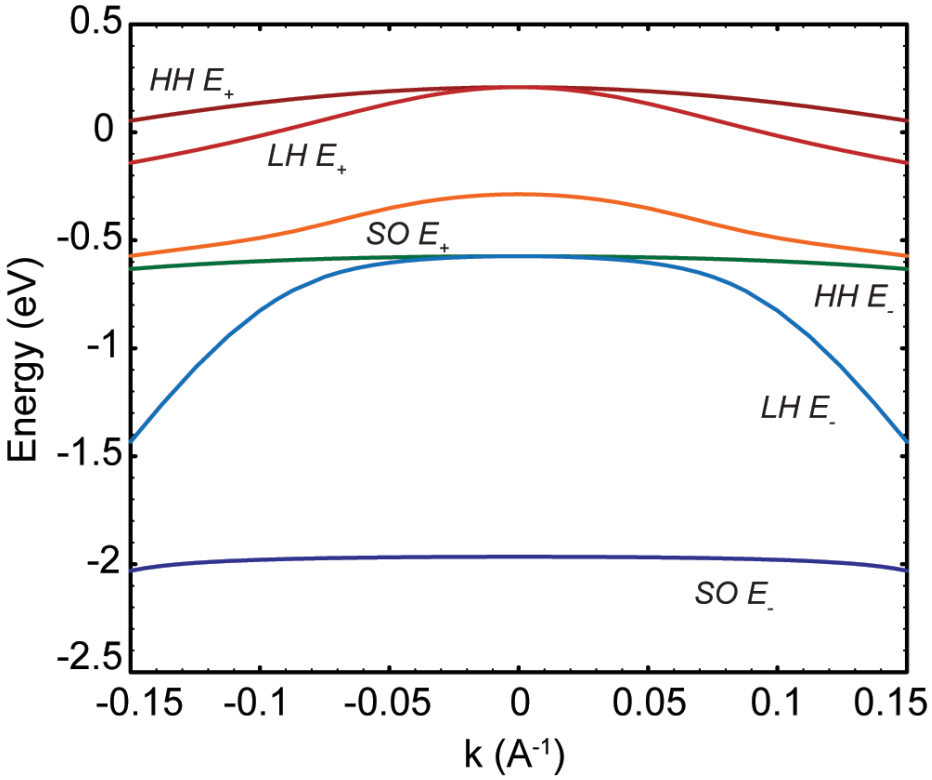
Fig 2. Photomodulated reflectance spectra of several $GaBi_xAs_{1-x}$ films ranging in composition ($0<x<0.084$). Each spectrum contains features associated with the bandgap (E_g) and spin-orbit split-off to conduction band ($E_g + \Delta_0$) optical transitions in the GaAs capping layer, while those films with compositions $x>0$ also exhibit transitions related to the heavy and light hole E_+ to conduction band transition (*HH/LH* E_+) and spin-orbit split-off E_+ to conduction band transitions ($E_g + \Delta_0^+$) in the $GaBi_xAs_{1-x}$ film.

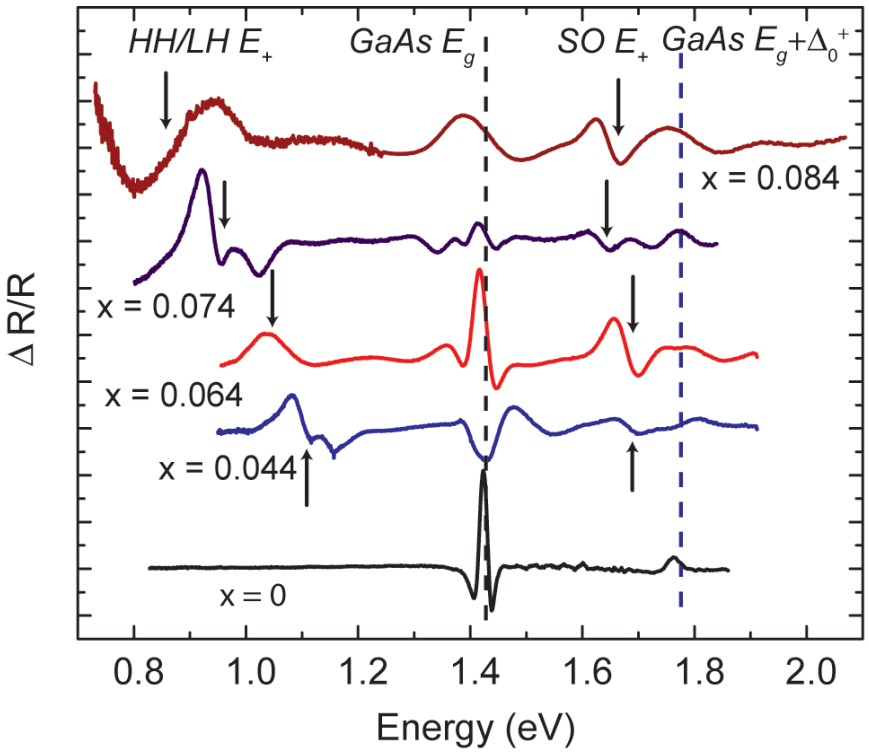
Fig 3. (a) Experimental E_g and $E_g + \Delta_0$ transition energies measured by PR along with the dependencies predicted by the VBAC model. (b) VBAC-determined composition dependence of the valence band edge positions. (c) Measured and theoretically predicted composition dependence of the bandgap and spin-orbit splitting energies in $GaBi_xAs_{1-x}$. The symbols refer to the same data presented in (a).

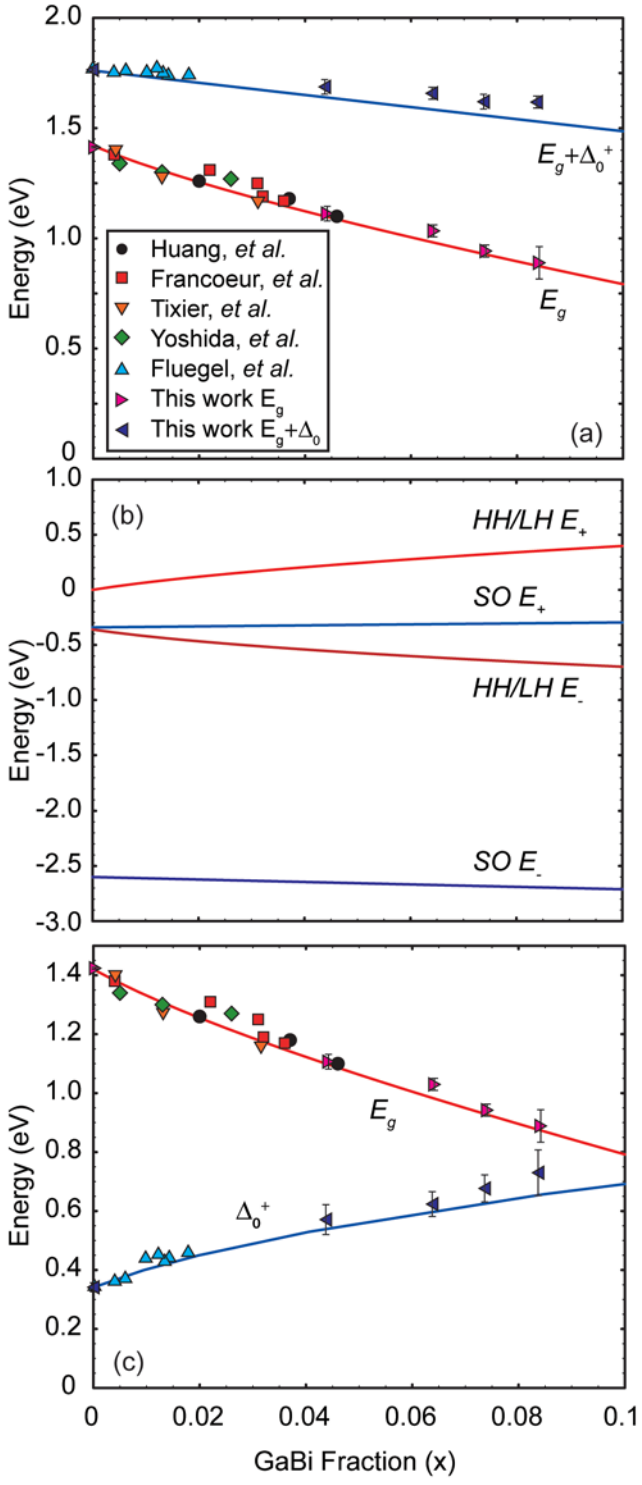
TABLE AND TABLE CAPTION

x	E_g (eV)	Γ_{Eg} (eV)	$E_g + \Delta_0$ (eV)	$\Gamma_{Eg+\Delta 0}$ (eV)	Δ_0 (eV)
0	1.43	0.01	1.77	0.02	0.34
0.044	1.11	0.05	1.68	0.05	0.57
0.064	1.04	0.04	1.68	0.04	0.64
0.074	0.94	0.04	1.63	0.05	0.69
0.084	0.88	0.12	1.64	0.04	0.76

Table 1. Energies (E) and broadening parameters (Γ) used to fit the bandgap (E_g) and spin-orbit split-off band to conduction band ($E_g + \Delta_0$) transitions in the PR spectra shown in Fig. 2. Also displayed is the spin-orbit splitting energy (Δ_0) for each composition.


0.5
0
-0.5
-1
-1.5
-2
-2.5
Energy (eV)
-0.15
-0.1
-0.05
0
0.05
0.1
0.15
k (A-1)
HH E+
LH E+
SO E+
HH E-
LH E-
SO E-


HH/LH E_+
GaAs E_g
SO E_+
GaAs $E_g+\Delta_0^+$
x = 0.084
x = 0.074
x = 0.064
x = 0.044
x = 0
Δ R/R
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Energy (eV)


Energy (eV)
2.0
1.5
1.0
0.5
0
$E_g+\Delta_0^+$
E_g
Huang, et al.
Francoeur, et al.
Tixier, et al.
Yoshida, et al.
Fluegel, et al.
This work E_g
This work $E_g+\Delta_0$
(a)
(b)
HH/LH E_+
SO E_+
HH/LH E_-
SO E_-
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
(c)
1.4
1.2
0.8
0.6
0.4
0.2
Δ_0^+
0.02
0.04
0.06
0.08
0.1
GaBi Fraction (x)