

Contactless electroreflectance study of E0 and E0+SO transitions in In_{0.53}Ga_{0.47}Bi_xAs_{1-x} alloys

R. Kudrawiec, J. Kopaczek, J. Misiewicz, J. P. Petropoulos, Y. Zhong, and J. M. O. Zide

Citation: [Applied Physics Letters](#) **99**, 251906 (2011); doi: 10.1063/1.3669703

View online: <http://dx.doi.org/10.1063/1.3669703>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/99/25?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[A combined capacitance-voltage and hard x-ray photoelectron spectroscopy characterisation of metal/Al₂O₃/In_{0.53}Ga_{0.47}As capacitor structures](#)

J. Appl. Phys. **116**, 024104 (2014); 10.1063/1.4887517

[Temperature dependence of E₀ and E₀ + SO transitions in In_{0.53}Ga_{0.47}Bi_xAs_{1-x} alloys studied by photoreflectance](#)

J. Appl. Phys. **112**, 113508 (2012); 10.1063/1.4768262

[Unusual broadening of E₀ and E₀ + SO transitions in GaAsBi studied by electromodulation spectroscopy](#)

J. Appl. Phys. **111**, 066103 (2012); 10.1063/1.3692763

[Contactless electroreflectance of optical transitions in tunnel-injection structures composed of an In_{0.53}Ga_{0.47}As / In_{0.53}Ga_{0.23}Al_{0.24}As quantum well and InAs quantum dashes](#)

J. Appl. Phys. **108**, 086106 (2010); 10.1063/1.3483948

[Effect of Er dopant on the properties of In_{0.53}Ga_{0.47}As layers grown by liquid phase epitaxy](#)

J. Appl. Phys. **81**, 2391 (1997); 10.1063/1.364243



AIP | Journal of
Applied Physics

Journal of Applied Physics is pleased to
announce **André Anders** as its new Editor-in-Chief

Contactless electroreflectance study of E_0 and $E_0 + \Delta_{SO}$ transitions in $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ alloys

R. Kudrawiec,^{1,a)} J. Kopaczek,¹ J. Misiewicz,¹ J. P. Petropoulos,² Y. Zhong,³ and J. M. O. Zide³

¹*Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

²*Department of Electrical and Computer Engineering, University of Delaware, Newark, Delaware 19716, USA*

³*Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716, USA*

(Received 11 October 2011; accepted 23 November 2011; published online 21 December 2011)

Energies of E_0 and $E_0 + \Delta_{SO}$ transitions in $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ alloys with $0 < x \leq 0.036$ have been studied by contactless electroreflectance spectroscopy at room temperature. It has been clearly observed that the E_0 transition shifts to longer wavelengths (~ 50 meV/% of Bi), while the $E_0 + \Delta_{SO}$ transition is approximately unchanged with changes in Bi concentration. These changes in the energies of optical transitions are discussed in the context of the valence band anticrossing model as well as the common anion rule applied to III-V semiconductors. © 2011 American Institute of Physics. [doi:10.1063/1.3669703]

$\text{GaBi}_x\text{As}_{1-x}$ with a few percent of Bi atoms (dilute bismuthides) has attracted attention because of its interesting fundamental properties,^{1–10} including a large bandgap reduction (~ 80 – 90 meV/% of Bi) and a strong enhancement of the spin-orbit splitting due to the incorporation of Bi atoms. Very similar effects are expected when Bi atoms are incorporated into $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ (lattice-matched to an InP substrate). In this material, much narrower energy gaps can be reached since the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ host has a smaller bandgap than the GaAs host (0.75 eV versus 1.42 eV at 300 K).¹¹ Also, it is expected that the incorporation of Bi atoms into $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ alloy should enhance the spin-orbit splitting, but experimental studies on the spin-orbit splitting in $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ have not been reported.

The spin-orbit splitting for $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ is technologically important because, for typical III-V alloys deposited on InP substrates (InGa(Al)As and InGaAsP alloys with small strain, $|\epsilon| < 1\%$), the energy gap is larger than the spin-orbit splitting.¹¹ This condition enhances Auger processes in the valence band, which unfavorably influence the performances of InP-based lasers. This problem becomes very significant for InP-based lasers emitting at longer wavelengths since energy gap in the active region of such lasers becomes similar to the spin-orbit splitting.¹² It is expected that engineering the bandgap and spin-orbit splitting in InGaBiAs alloys can suppress Auger processes in the valence band. In this context, experimental studies of the energy gap and the spin-orbit splitting in InGaBiAs alloys are necessary and very important.

To date, only a few papers study InGaBiAs alloys,^{13,14} and only one reports bandgap measurements.¹⁴ None of these previous reports include contactless electroreflectance (CER) or photoreflectance measurements. CER spectroscopy, due to its differential and absorption-like character, is an excellent technique to study the energy gap and the spin-orbit splitting in III-V semiconductors. In this letter, we use CER spectroscopy to study the fundamental bandgap (E_0) and the

spin-orbit split ($E_0 + \Delta_{SO}$) transitions in $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ alloys with $0 < x \leq 0.036$. Measuring the energies of the two transitions, we were able to determine the Bi-related enhancement of spin-orbit splitting in this alloy as well as the Bi-related narrowing of the energy gap. The obtained results have been discussed in the context of the valence band anticrossing (VBAC) model⁷ and the common anion rule applied in III-V semiconductors.¹⁵

$\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layers were grown on (100)-oriented InP:Fe substrates by molecular beam epitaxy using solid sources of In, Ga, and Bi, and a valved arsenic cracker. Prior to the growth of $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layer, a 50 nm lattice-matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ buffer layer was deposited to achieve a clean epitaxial surface. It has been determined by using x-ray diffraction and Rutherford backscattering spectroscopy that the thickness of $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layers is in the range of 200–700 nm (which does not impact the CER measurement), and Bi concentration is varied from 1.1% to 3.6%. Relevant details on the growth conditions and structural investigations are described in Ref. 14.

CER spectra were measured using the “bright” configuration of the experimental set-up described elsewhere.¹⁶ The samples were mounted in a capacitor with the top electrode made from a copper-wire mesh which is semi-transparent to light. This electrode was kept at a distance of ~ 0.5 mm from the sample surface, while the sample itself was fixed on the bottom copper electrode. A maximum peak-to-peak alternating voltage of ~ 3.0 kV with frequency 285 Hz was applied. Phase sensitive detection of CER signal was accomplished using a lock-in amplifier. Thermoelectrically cooled InGaAs and InAs detectors were applied in the range of 1.0–1.6 and 1.6–2.8 μm , respectively. An edge filter with cut off at ~ 1.6 μm was used to eliminate the second order of diffraction during measurements in the 1.6–2.8 μm spectral range. Other relevant details of CER measurements are described elsewhere.^{16,17}

Figures 1 and 2 show room temperature CER spectra measured in the vicinity of E_0 and $E_0 + \Delta_{SO}$ transitions, respectively, for $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layers with $0 < x \leq 0.036$.

^{a)}Electronic mail: robert.kudrawiec@pwr.wroc.pl.

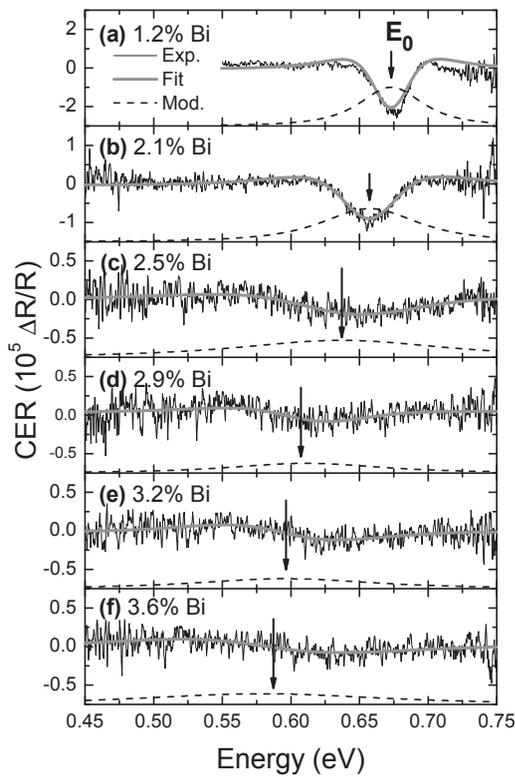


FIG. 1. Room temperature contactless electroreflectance spectra of $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layers in the vicinity of the E_0 transition.

It is clearly visible that the E_0 transition shifts to longer wavelengths with the increase in Bi concentration, while the $E_0 + \Delta_{\text{SO}}$ is observed to always be at the same energy within the experimental error. In order to extract energies of E_0 and $E_0 + \Delta_{\text{SO}}$ transitions, CER spectra have been fitted by Aspnes formula,¹⁸

$$\frac{\Delta R}{R}(E) = \text{Re}[C e^{i\vartheta} (E - E_j + i\Gamma)^{-m}], \quad (1)$$

where $\frac{\Delta R}{R}(E)$ is the energy dependence of CER signal, C and ϑ are the amplitude and phase of the line, and E_j and Γ are the energy and the broadening parameter of the optical transition, respectively. The term m depends on the type of optical transition. For an inhomogeneous system, it can be assumed that $m=3$. The fitting curves are shown as thick grey lines in Figs. 1 and 2 together with the moduli of CER resonances which are shown as dashed lines. The modulus of CER resonance (ρ) was obtained according to Eq. (2) with parameters taken from the fit.

$$\Delta\rho(E) = \frac{|C|}{[(E - E_j)^2 + \Gamma^2]^{\frac{m}{2}}}. \quad (2)$$

Figure 3 shows the energies of E_0 and $E_0 + \Delta_{\text{SO}}$ transitions for $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layers extracted from the fitting procedure together with the spin-orbit splitting Δ_{SO} calculated from this data. It is clearly visible that the energy gap narrows and the spin-orbit splitting increase with the increase in Bi concentration. For $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layers with $\text{Bi} > 3\%$, the spin-orbit splitting became comparable with the energy gap. In GaAsBi alloys, a similar situation was

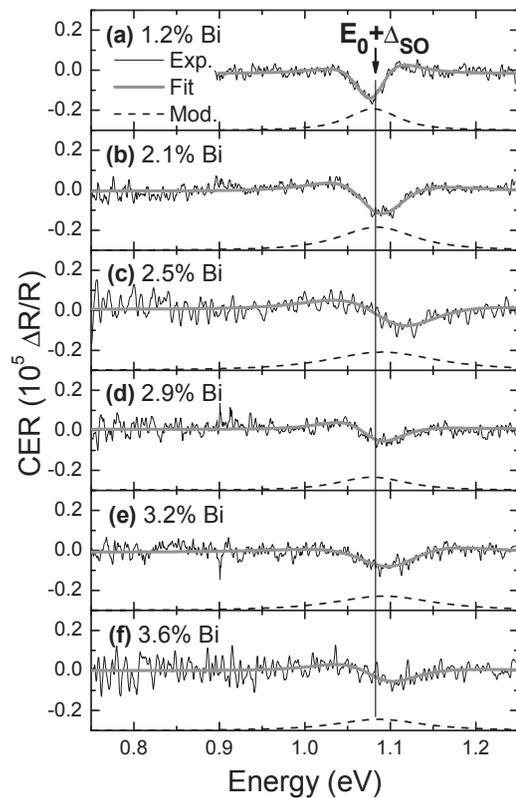


FIG. 2. Room temperature contactless electroreflectance spectra of $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ layers in the vicinity of the $E_0 + \Delta_{\text{SO}}$ transition.

observed for $\sim 10\%$ of Bi atoms.⁷ For $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ alloys, this effect is observed at lower Bi concentration due to the narrower energy gap of the host. It is also worth noting that the Bi-related reduction of the energy gap for this alloy has been found to be ~ 50 meV/% of Bi atoms, which is smaller than for GaAs host (~ 80 - 90 meV/% of Bi atoms), but consistent with results found by previous measurements.¹⁴ Taking into account the *ab initio* self-consistent calculations for III-Bi compounds,¹⁹ one might expect that Bi-related reduction of energy gap should be larger for an

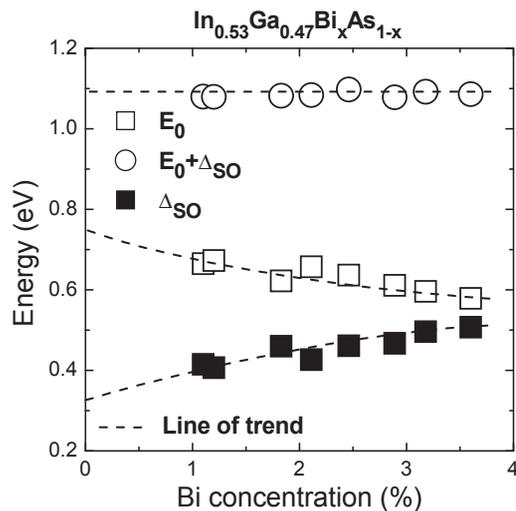


FIG. 3. Energies of E_0 (open squares) and $E_0 + \Delta_{\text{SO}}$ (open circles) transitions in $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ of various Bi concentrations extracted from contactless electroreflectance measurements. The spin-orbit splitting (solid squares) in $\text{In}_{0.53}\text{Ga}_{0.47}\text{Bi}_x\text{As}_{1-x}$ alloy obtained from the measurements of E_0 and $E_0 + \Delta_{\text{SO}}$ transitions.

In_{0.53}Ga_{0.47}As host than for a GaAs host because of the calculated energy gap of InBi and GaBi (−4.75 and −2.91 eV, respectively).²⁰ The obtained experimental data suggest that this simple virtual crystal approximation does not work for this alloy. Therefore, the empirical VBAC model⁷ is more useful to describe the energy gap dependence. This is similar to the (conduction band) anti-crossing results observed in dilute nitrides.²¹ However, it is also a reasonable first approximation to say the Bi-related reduction of the energy gap in this alloy can be given by a linear function with the slope of −50 meV/% Bi.

We have found that for In_{0.53}Ga_{0.47}Bi_xAs_{1−x}, the Bi-related band gap narrowing and the increase in spin-orbit splitting are equal in magnitude within the experimental error. This observation can be explained by a shift of the heavy/light hole band towards the conduction band without any shifts of the conduction and/or the spin-orbit splitted band as illustrated schematically in Fig. 4. Such changes in the band structure of In_{0.53}Ga_{0.47}As host are in agreement with the VBAC model,⁷ which assumes that Bi atoms influence only the valence band.

Finally, it is also worth noting that the observed changes in the energy gap and the spin orbit splitting are in agreement with the common anion rule applied in III-V semiconductors. According to this rule, the valence-band nature of III-V semiconductors can be characterized primarily by the anion (V) species, while the conduction band can be explained primarily by the cation (III) species. The spin-orbit splitting, therefore, changes very significantly with changes in anion species. For example, the spin-orbit splittings in Ga-V (GaP, GaAs, GaSb, and GaBi) are 0.08, 0.34, 0.76, (Ref. 11) and ∼2.1 eV,²⁰ respectively. In In-V (InP, InAs, InSb, and InBi), the spin-orbit splitting are 0.11, 0.39, 0.81, (Ref. 11) and ∼2.1 eV,²⁰ respectively. The energy gap decreases when lighter anions are replaced by heavier ones. According to these trends, the incorporation of heavier Bi anions into In_{0.53}Ga_{0.47}As host influences its valence band so that the energy gap is decreased and the spin-orbit splitting is increased. Taking into account the experimental result that the energy of $E_0 + \Delta_{SO}$ transition is almost the same for all samples (see Fig. 2), this means that Bi incorporation into

In_{0.53}Ga_{0.47}As host causes the heavy/light hole band to shift towards the conduction band, while the spin-orbit split band largely does not shift, as shown in the sketch in Fig. 4.

In conclusion, it has been clearly shown that the incorporation of Bi atoms into In_{0.53}Ga_{0.47}As host causes band gap reduction and modification of the spin-orbit splitting. These changes in the band structure are caused by a shift of heavy- and light-hole bands towards the conduction band. This means that the valence band of these materials can be tuned independently of the bandgap (through accompanying changes in cation), and the relation between the energy gap and the spin-orbit splitting in In_{0.53}Ga_{0.47}Bi_xAs_{1−x} can be tuned from one typical of InGaAlAs and InGaAsP alloys grown on InP substrate ($E_0 > \Delta_{SO}$) to an unusual relation for III-V/InP structures where the energy gap is very close to the spin-orbit splitting ($E_0 \approx \Delta_{SO}$). This allows the enhanced control of optoelectronic devices grown on InP substrate.¹²

R.K. acknowledges the support within the “IUVENTUS PLUS” grant. Y.Z., J.P.P., and J.M.O.Z. acknowledge the support of the U.S. Office of Naval Research.

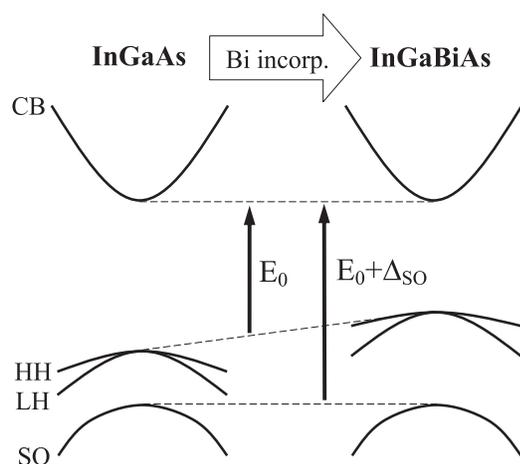


FIG. 4. Sketch of Bi-related changes in the band structure of In_{0.53}Ga_{0.47}Bi_xAs_{1−x} alloys: CB—conduction band, HH—heavy-hole band, LH—light-hole band, and SO—spin-orbit splitted band.

- ¹K. Oe and H. Okamoto, *Jpn. J. Appl. Phys., Part 2* **37**, L1283 (1998).
- ²J. Yoshida, T. Kita, O. Wada, and K. Oe, *Jpn. J. Appl. Phys.* **42**, 371 (2003).
- ³S. Tixier, M. Adamczyk, T. Tiedje, S. Francoeur, A. Mascarenhas, P. Wei, and F. Schiettekatte, *Appl. Phys. Lett.* **82**, 2245 (2003).
- ⁴S. Francoeur, M. J. Seong, A. Mascarenhas, S. Tixier, M. Adamczyk, and T. Tiedje, *Appl. Phys. Lett.* **82**, 3874 (2003).
- ⁵B. Fluegel, S. Francoeur, A. Mascarenhas, S. Tixier, E. C. Young, and T. Tiedje, *Phys. Rev. Lett.* **97**, 067205 (2006).
- ⁶K. Bertulis, A. Krotkus, G. Aleksejenko, V. Pacebutas, R. Adomavicius, G. Molis, and S. Marcinkevicius, *Appl. Phys. Lett.* **88**, 201112 (2006).
- ⁷K. Alberi, O. D. Dubon, W. Walukiewicz, K. M. Yu, K. Bertulis, and A. Krotkus, *Appl. Phys. Lett.* **91**, 051909 (2007).
- ⁸M. Henini, J. Ibanez, M. Schmidbauer, M. Shafi, S. V. Novikov, L. Turyanska, S. I. Molina, D. L. Sales, M. F. Chisholm, and J. Misiewicz, *Appl. Phys. Lett.* **91**, 251909 (2007).
- ⁹R. Kudrawiec, P. Poloczek, J. Misiewicz, M. Shafi, J. Ibanez, R. H. Mari, M. Henini, M. Schmidbauer, S. V. Novikov, L. Turyanska *et al.*, *Microelectron. J* **40**, 537 (2009).
- ¹⁰G. Pettinari, A. Polimeni, M. Capizzi, J. H. Blokland, P. C. M. Christianen, J. C. Maan, E. C. Young, and T. Tiedje, *Appl. Phys. Lett.* **92**, 262105 (2008).
- ¹¹I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, *J. Appl. Phys.* **89**, 5815 (2001).
- ¹²S. J. Sweeney, Z. Batool, K. Hild, S. R. Jin, and T. J. C. Hosea, *The Potential Role of Bismide Alloys in Future Photonic Devices* in ICTON 2011 (IEEE, New York, 2011).
- ¹³G. Feng, M. Yoshimoto, K. Oe, A. Chayahara, and Y. Horino, *Jpn. J. Appl. Phys.* **44**, 1161 (2005).
- ¹⁴J. P. Petropoulos, Y. Zhong, and J. M. O. Zide, *Appl. Phys. Lett.* **99**, 031110 (2011).
- ¹⁵S. Adachi, *Properties of Semiconductor Alloys: Group-IV, III-V and II-VI Semiconductors* (Wiley, Chichester, 2009).
- ¹⁶R. Kudrawiec and J. Misiewicz, *Rev. Sci. Instrum.* **80**, 096103 (2009).
- ¹⁷R. Kudrawiec, *Phys. Status Solidi B* **247**, 1616 (2010).
- ¹⁸D. E. Aspnes, *Surf. Sci.* **37**, 418 (1973).
- ¹⁹M. Ferhat and A. Zaoui, *Phys. Rev. B* **73**, 115107 (2006).
- ²⁰It is worth noting that calculations within the local density approximation give the energy gap −1.45 eV for GaBi: A. Janotti, S.-H. Wei, and S. B. Zhang, *Phys. Rev. B* **65**, 115203 (2002). Recent calculations of InBi and GaBi give the energy gap of −1.5 and −1.7 eV, respectively, and the spin-orbit splitting of ∼2.1 eV for the two compounds: S.-H. Wei, *Band Structures of Bi Containing Isovalent III-V Alloys and the Validity of the Band Anticrossing Model*, International workshop on bismuth-containing semiconductors: Theory, simulations and experiment, Surrey, UK, 18–20 July (2011). <http://www.bismides.net/>
- ²¹W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.* **82**, 1221 (1999).