

Bi isoelectronic impurities in GaAsS. Francoeur,^{1,2,*} S. Tixier,³ E. Young,³ T. Tiedje,³ and A. Mascarenhas²¹*École Polytechnique de Montréal, Montréal, Québec, Canada H3C 3A7*²*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*³*AMPEL, Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z4*

(Received 9 October 2007; published 25 February 2008)

GaAs_{1-x}Bi_x is a mixed-anion semiconductor alloy. In the As-rich regime ($0.4\% < x < 4\%$), isovalent Bi creates a series of bound states but this alloy nonetheless exhibits properties characteristic of regular semiconductors. The dual impurity-alloy character can be tuned by varying the temperature. Below 100 K, multiple Bi bound states appear at low energy in the luminescence spectrum. These states are associated with the pseudo-donor potential created by isovalent Bi impurities. Taking into consideration the concentration regime at which these bound states are observed, they likely involve excitons bound to clusters composed of a few substitutional Bi atoms, indirectly implying that the isolated Bi state is resonant with the valence band. At ambient temperature, these localized states are strongly suppressed and luminescence from the band edges is measured. The important Bi-induced atomic disorder creates a strong intraband coupling resulting in an important reduction of the band gap for a relatively small alloy concentration. These results on a pseudodonor isoelectronic alloy are reminiscent of the better known pseudoacceptor GaAsN, but offer a complementary view of this intriguing and yet little understood class of alloys.

DOI: [10.1103/PhysRevB.77.085209](https://doi.org/10.1103/PhysRevB.77.085209)

PACS number(s): 78.55.Cr, 71.55.Eq, 78.20.-e

Semiconductor materials made of isoelectronic impurities¹ form a small and little understood group of alloys exhibiting atypical electronic characteristics. For example, N in GaAs reduces both the band gap and the lattice constant, resulting in an unusual band gap dependence as a function of nitrogen concentration.² More generally, these alloys show a number of unusual characteristics that have raised interest as, technologically, they extend the functionality of semiconductor materials and, scientifically, they offer an opportunity to refine our understanding of alloy and impurity physics.³ It is now understood that their remarkable properties stem from the seemingly paradoxical dual impurity-alloy role that the isovalent impurity plays: (1) it creates localized states in the band gap that are easily noticeable at low concentration and low temperature,⁴⁻⁶ and (2) it redefines the interaction between electronic bands and results in highly perturbed alloy states.⁷⁻⁹ Studies of isoelectronic alloys have been largely limited to pseudoacceptor impurities, but large atoms have also been shown to produce isoelectronic traps^{10,11} and can, therefore, provide a valuable insight into the physics governing this class of highly perturbed semiconductors that is referred to as *isoelectronic alloys*.

In this paper, we present the necessary evidence demonstrating that GaAsBi is an isoelectronic alloy. We first show that Bi is an isoelectronic impurity in GaAs: at low concentration and low temperature, we show that few-atom Bi clusters create localized bound states. Second, we show that GaAs_{1-x}Bi_x ($x < 4\%$) exhibits important characteristics of an alloy, such as showing a well-defined band gap originating from extended electronic states. This paper is organized as follows: We first give a general description of isoelectronic impurities, then present photoluminescence results from GaAs doped with various concentrations of bismuth and discuss these results.

Semiconductor alloys are simply formed by isovalent atomic substitution. Whereas this isovalent impurity always

creates a perturbation to the host band structure, this perturbation, usually small, produces an energetically shallow and delocalized state that remains unnoticeable.¹² However, if the isovalent impurity and the atom it replaces have rather distinct characteristics, the impurity can create an important perturbation and, if strong enough, trap a charge carrier and significantly alter the properties of the host semiconductor. This difference in behavior can be understood by examining the difference between the intrinsic properties of the host atom and that substituting it. A large difference in atomic size and core potential produces a significant disruption of the electronic charge distribution, thus creating a highly localized center attractive to one type of carrier via a short-range potential.¹³ Isovalent impurities creating bound states are generally referred to as isoelectronic impurities; impurities attractive to electrons and holes are labeled pseudoacceptors and pseudodonors, respectively. The trapped carrier can subsequently bind a carrier of opposite charge via Coulombic interaction and form a bound exciton. Nitrogen in GaP and GaAs remains the most studied isoelectronic impurity in III-V alloys. The local redistribution of the electronic charge density around the nitrogen impurity creates a short-range potential attractive to electrons.¹³ Furthermore, two nearby isoelectronic impurities can also bind excitons,¹ but with a binding energy set by the separation between the nitrogen atoms and their respective orientation. Recently, in the study of GaAs_{1-x}N_x alloys, higher order nitrogen configurations have been found to trap excitons.^{14,15} Interestingly, these cluster states dominate the low-temperature luminescence, but an alloy with a well-defined, although perturbed, band gap is formed.^{9,16} This dual behavior of isoelectronic impurities is key to understanding these alloy systems and, conversely, can be used to identify isoelectronic alloys.

Much less attention has been given to pseudodonor isoelectronic impurities. Bismuth is the heaviest element of the III-V subgroup of semiconductors. Like nitrogen, the size and core electronic structure of Bi are significantly different

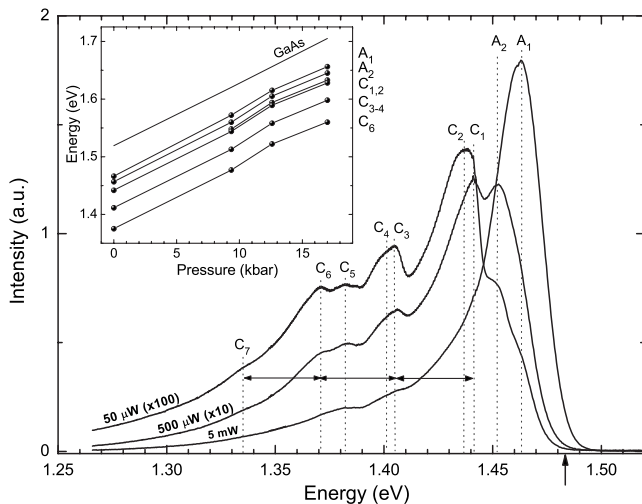


FIG. 1. Photoluminescence of $\text{GaAs}_{1-x}\text{Bi}_x$ with $x=0.4\%$ measured at 9 K at different excitation intensities. Inset: Energy of A_{1-2} , C_{1-4} , and C_6 as a function of hydrostatic pressure at 4.2 K. The vertical and horizontal arrows indicate the expected position of the band gap and the energy corresponding to LO phonons (~ 36 meV).

from those of P and As. In comparison to As, the core potential of Bi is markedly different as it has 50 more core electrons, most of them distributed in two additional d shell and one new f shell. Bi, indeed, forms pseudodonor bound states in GaP and InP located above the valence band maximum.^{10,17} These early studies have been limited to relatively small concentrations of 10^{17} cm^{-3} and, possibly for that reason, no pair or cluster states have been reported. From a scientific point of view, Bi doping of GaAs is likely to offer different insights into the physics of isoelectronic doping. We next present the study of gap states related to Bi in GaAs and demonstrate that Bi-localized states are observed, satisfying the first criteria to establish GaAsBi as an isoelectronic alloy.

The samples studied were grown by molecular beam epitaxy on GaAs. The GaAsBi layers are between 0.2 and 0.3 μm thick. Details on the growth conditions can be found in Ref. 18. The bismuth concentration was calculated from x-ray diffraction patterns using a GaBi lattice constant of 6.341 \AA extrapolated from Rutherford backscattering results.¹⁸ X-ray diffraction asymmetrical maps revealed that most of the samples were almost fully strained to match the GaAs substrate constant. The luminescence was excited with a 532 nm diode pumped solid state laser and detected with an InGaAs array detector.

Figure 1 shows the low-temperature luminescence of $\text{GaAs}_{1-x}\text{Bi}_x$ with $x=0.4\%$ for three excitation intensities. At all intensities, several sharp features positioned well below the gap of GaAs (1.519 eV) and that of $\text{GaAs}_{0.996}\text{Bi}_{0.004}$ (1.486 eV, measured from electroreflectance¹⁹ at 80 K and extrapolated to 4 K) are observed. The C_i features do not resemble any of the extrinsic radiative recombination commonly seen in GaAs.²⁰ The respective intensity of the peaks observed is very sensitive to the excitation intensity and, as expected, the saturation of deeper levels promotes the lumi-

nescence of higher energy centers. Peaks C_3 , C_4 , C_6 , and C_7 appear to be LO phonon replicas of C_1 and/or C_2 and, after proper background correction, exhibit a constant integrated intensity ratio. The presence of three phonon replica indicates an important electron-phonon coupling. The transition probability from the n vibronic level to the zeroth vibronic level is given by $I_{n0} = e^{-S} S^n / n!$, where S represents the most probable number of phonon participating in the optical transition. Using this relationship to model the intensity of C_{1-2} , C_{3-4} , C_6 , and C_7 , we find $S=0.7$. This value is somewhat lower than that measured for GaP:Bi $S=2.5-3.0$,²¹ but is, nonetheless, much higher than that of donor-acceptor transitions or other effective mass impurity ($S < 0.1$).²⁰ Such a large number of phonon replicas is typically observed from deep impurities: as the binding energy increases, the spatial localization of the carrier is important and its interaction with lattice vibrations becomes stronger. It is interesting to note that the zero phonon lines C_1 and C_2 show an intermediate binding energy (45 and 50 meV), but with a considerable electron-phonon coupling. This behavior is typical of an isoelectronic impurity and originates from the very narrow and steep potential it creates. The only other impurity or defect emitting around the positions of C_1 and C_2 is the gallium antisite at 1.441 eV.²²⁻²⁴ However, the transition probability for the simultaneous emission of a phonon is much lower than what is observed here.²³ This alternative origin can, therefore, be ruled out.

It is reasonable to expect that Bi behaves as an isoelectronic impurity in GaAs as the Bi $6p$ orbital is substantially higher than the As $4p$ orbital.²⁵ However, similar to the case of the isolated nitrogen level in GaAs, the absolute positions of the bands need to be considered. Early theoretical works have concluded that an isolated Bi impurity does not form a bound state in GaAs.^{26,27} More recently, two theoretical calculations have been reported, but opposite conclusions were reached. The first finds a Bi level 180 meV above the valence band of GaAs.²⁸ The second reveals a resonant state approximately 80 meV below the valence band maximum.²⁵ This second result appears more realistic, since by considering the absolute energy of the isolated Bi level measured in GaP,¹⁰ InP,¹⁷ and AlAs, and by considering the natural band alignment²⁹ between these binaries and GaAs, it appears that Bi should form a resonant state in the valence band of GaAs.

The following analysis, indeed, indicates that the isolated Bi level is, indeed, resonant within the valence band. It is relatively easy to saturate the luminescence from C_1 and C_2 , and, at high excitation, two additional transitions appear, A_1 and A_2 . These transitions do not show a large electron-phonon coupling and are, therefore, not related to Bi impurities. Their binding energies of 25 and 37 meV are similar to those of C and Si acceptors,³⁰ whose unintentional incorporation, revealed by secondary ion mass spectrometry, is at the level of $10^{16}-10^{17} \text{ cm}^{-3}$. Assuming that A_1 and A_2 are acceptor-related transitions, we can estimate the relative concentration of the centers giving rise to C_i transitions. Since C_1 and C_2 saturate before A_1 and A_2 , their concentrations are unlikely to significantly exceed those of A_1 and A_2 . Now, by assuming a random distribution of Bi atoms, the concentrations of isolated Bi atom, nearest-neighbor pairs, and triplets are 8.2×10^{19} , 4×10^{18} , and $1.1 \times 10^{17} \text{ cm}^{-3}$, respectively. It,

therefore, appears unlikely that the Bi-related excitons observed originate from isolated Bi atoms. Furthermore, we note that the range of concentrations at which these luminescent features are observed is at concentrations exceeding 10^{19} cm^{-3} : had isolated atoms been involved, their luminescence should have been observable at much lower concentrations ($\sim 10^{17} \text{ cm}^{-3}$). This finding suggests that the Bi isolated state is not located inside the forbidden band gap and is, therefore, likely resonant with the valence band, contradicting the recent work of Janotti *et al.*,²⁸ but supporting that of Zhang *et al.*²⁵ This behavior is similar to that of nitrogen in GaAs, where the isolated N state and most pair states are resonant with the conduction band,³¹ only two pair states of low interatomic separation^{5,32,33} and cluster states (three atoms or more) are located in the band gap of GaAs.^{14,15} Our analysis of the intensity of C_i centers suggests that few-atom clusters are involved, but the exact number of atoms is difficult to evaluate. A detailed study of the configuration of these clusters is under way.

In contrast to pseudoacceptor states, the pressure coefficient of Bi states is very similar to that of the band gap. The inset of Fig. 1 shows the energy position of A_i and C_i states as a function of hydrostatic pressure. As can be seen, the dependence of the luminescence energy of the excitonic bound states closely follows that of the GaAs band edge, which increases at a rate of 10.8 meV/kbar .³⁴ It is important to note that most of the increase in GaAs is accommodated by an upward shift of the conduction band,³⁵ the pressure coefficient of the valence being a small fraction of the overall shift. For a Bi-bound hole, the pressure coefficient is mostly determined by valence band states associated with a low deformation potential, hence the bound exciton should shift at a rate similar to that of the conduction band minimum. Accordingly, we observe a shift of $11.1 \pm 0.4 \text{ meV/kbar}$.³⁹ It is interesting to note that the Bi resonant state could only be observed if the valence band maximum moved downward with increasing pressure. However, Zhang *et al.* have calculated that the isolated Bi state should stay resonant at all pressures.²⁵

The luminescence intensity of these localized centers is very sensitive to temperature as high-energy centers have a low activation energy and quickly ionize as temperature increases. Figure 2 shows the luminescence measured at 50 K for the sample presented in Fig. 1. At this temperature, C_1 and C_2 and their phonon replicas do not dominate the spectrum and lower energy features, strongly saturated at 9 K, become dominant due to their higher activation energy. The thermal energy rapidly weakens the effectiveness of strongly localized potentials to recombine excitons, as it has been observed for the case of nitrogen in GaAs.⁶ Instead, zero-phonon lines with binding energies of up to 120 meV originating from low-density higher-order Bi clusters are observed. As for previous centers, their exact atomic configuration is unknown, but it is reasonable to expect that these lower density clusters have a larger number of Bi atoms, making them statistically unfavorable configurations. At 77 K and higher temperatures, all bound excitonic states disappear and a different transition, quenched at low temperatures, appears around 100 K. As this transition shifts with temperature at a rate identical to that of the GaAs band gap,³⁶

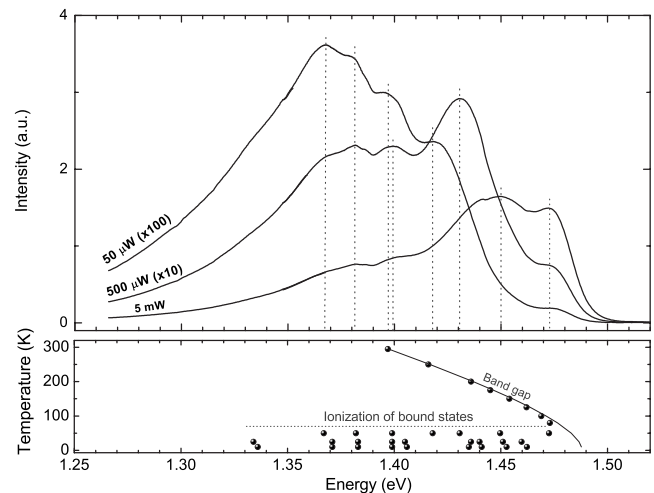


FIG. 2. Top panel: Photoluminescence of $\text{GaAs}_{1-x}\text{Bi}_x$ with $x = 0.4$ measured at 50 K. Bottom panel: Energy of bound states as a function of temperature. The solid line represents a fit of the type $E(0) - \alpha T^2 / (T + \beta)$.

we associated this transition to the GaAsBi band gap. This assignment is also corroborated by electroreflectance measurements.¹⁹

Sub-band-gap Bi-related features are observed at all concentrations. Figure 3 shows the luminescence spectra obtained at 9 K with an excitation intensity of 1 mW on samples with concentrations up to 3.1%. For each concentration, the extrapolated value of the band gap at this temperature is shown by the vertical line. The discrete states observed at 0.4% concentration broaden and merge to form a wide luminescence band produced by Bi few-atom clusters. At higher bismuth concentration, the number of atoms in a given cluster increases, therefore producing states with an energy approaching that of the $6p$ orbital of Bi. The important broadening and overlapping are explained by the increasing statistical disorder of the Bi distribution, mutual in-

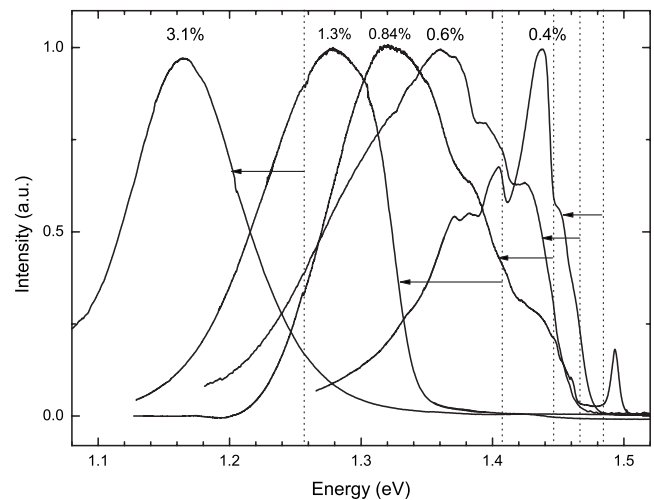


FIG. 3. Photoluminescence of $\text{GaAs}_{1-x}\text{Bi}_x$ with $x = 0.4\%$, 0.6% , 0.84% , 1.3% , and 3.1% measured at 9 K. The vertical lines indicate the position of the band gaps at these concentrations.

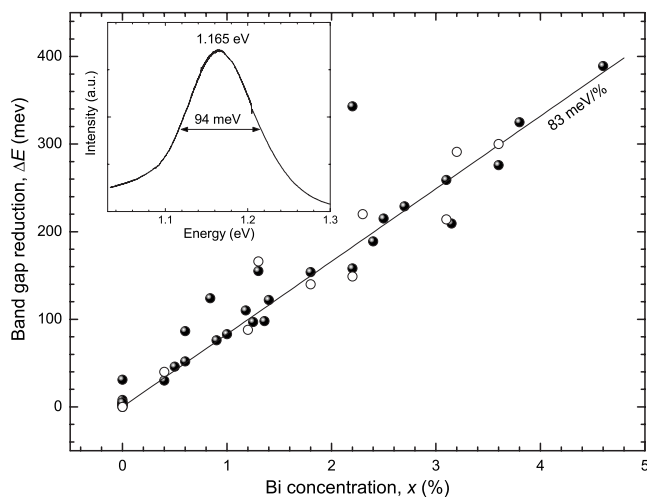


FIG. 4. Band gap energy reduction of $\text{GaAs}_{1-x}\text{Bi}_x$ with respect to that of GaAs, from room-temperature photoluminescence (●) and electroreflectance (○) from Ref. 19. The inset shows a 300 K PL spectrum for $x=2.3\%$.

teractions, and impurity band formation. The position of the luminescence peaks is very sensitive to excitation intensity. For samples with 1.3% and 3.1% concentrations, the luminescence peaks narrow and shift at the rates of 27 and 25 meV per decade of excitation intensity, respectively. All Bi-cluster-related luminescence disappear above 100 K and a transition associated with the GaAsBi band gap is observed.

Even though Bi-cluster states are omnipresent in the luminescence spectra obtained at low temperature, a behavior reminiscent of regular alloys is observed at higher temperatures. At 300 K, the full width at half maximum of the luminescence is broad (~ 100 meV at 2.5% in the set inset of Fig. 4), but the luminescence energy and line shape are insensitive to excitation intensity (up to 100 mW), indicating that all Bi-related bound states are ionized. A similar effect was observed in N doped GaAs.⁶ Figure 4 shows the band gap energy reduction $\Delta E [=E_0(\text{GaAs})-E_0(\text{GaAsBi})]$ obtained from photoluminescence and electroreflectance.¹⁹ As can be seen, these two techniques provide a very consistent measurement of the band gap and both indicate a rapid decrease of the band gap energy as a function of concentration. The compressive strain produced by the substrate lifts the degeneracy of the valence band states and the lowest energy transition, observed from low-excitation photoluminescence, involves the heavy-hole band. We find that the condition to heavy-hole transition drops at a rate of $(83 \pm 3 \text{ meV})/\%$ Bi, indicating a stress-free band gap reduction of $(88 \pm 3 \text{ meV})/\%$ Bi. This variation significantly exceeds the linearly interpolated value of 28 meV/% Bi, obtained using the calculated band gap of -1.45 eV for GaBi,²⁸ suggesting that this alloy is characterized by a large bowing coefficient. Although the measured variation is smaller than the band gap variation observed for GaAsN ($\sim 145 \text{ meV}/\% \text{ N}$), it is substantially larger than that of other mixed-anion GaAs-based alloys ($21 \text{ meV}/\% \text{ N}$ for GaAsSb and $15 \text{ meV}/\% \text{ N}$ for

GaAsP), indicating a behavior resembling that expected from an isoelectronic alloy. A deviation from the linearly interpolated transition energies, often characterized by the bowing coefficient, has been assigned to the atomic disorder unavoidably present in mixed alloys. Two effects contribute to disorder: the atomic lattice relaxation needed to preserve the bond lengths³⁷ and the chemical disparity between the internal electronic structure of the two atoms sharing the same sublattice. In contrast to crystals of known symmetry, the local charge distribution follows the distribution statistics and translational invariance is lost. The presence of disorder has very important effects on the electronic structures of the alloy: it introduces intraband and interband coupling.³⁸ Due to small energy separation, intraband coupling usually dominates and decreases the gap below the linearly interpolated value. The strength of this coupling is directly related to the amplitude of the charge density variation on the mixed sublattice and is proportional to the difference in core potential of the host atom and its substituent. Indeed, isoelectronic alloys exhibit a large bowing coefficient and other irregular characteristics, simply because the charge fluctuations reached unprecedented levels. Indeed, as demonstrated, few-atom Bi clusters create excited bound states easily observed at low temperature.

Although the effectiveness of the strongly localized potential associated with Bi clusters is suppressed at 300 K, its presence should significantly affect the mobility of holes. Additionally, due to the rapid band gap variation, the spectral linewidth of the band gap is expected to be considerably larger than other alloys. The broad luminescence observed at 300 K is attributed to natural compositional fluctuations which, on a scale of the probed volume ($>300 \mu\text{m}^3$), produce an effective inhomogeneous broadening.

In summary, we find that Bi in GaAs generates a large number of localized states at low temperature in all samples studied ($x < 4\%$). At low concentration, these states show a very strong electron-phonon interaction for a relatively small binding energy. In higher concentration samples, a wide luminescence band composed of several unresolved features, whose energy is very sensitive to excitation, is observed. These observations are typical of isoelectronic impurities. Taking into consideration the statistical density of one-, two-, and three-atom clusters, it appears that these states likely originate from few-atom clusters, suggesting that the isolated Bi level is resonant within the valence band. In sharp contrast to the low-temperature spectra, the 300 K luminescence is free of any bound states and its energy reproduces the band gap energy obtained from electroreflectance measurements. The highly nonlinear band gap dependence observed indicates the presence of disorder-induced intraband coupling generated by the Bi impurities. This behavior is similar to what is observed in nitrogen doped GaAs. Finally, GaAsBi is a highly perturbed alloy where Bi induces potential fluctuations strong enough to bind excitons at low temperature and redefines band interactions to produce a highly nonlinear band gap variation.

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