Compositional dependence of the exciton reduced mass in GaAs$_{1-x}$Bi$_x$ ($x=0$–$10\%$)

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We report the compositional dependence of the exciton reduced mass, $\mu_{\text{exc}}$, of GaAs$_{1-x}$Bi$_x$ in a very large Bi concentration range ($x=0$–$10.6\%$). Photoluminescence under high magnetic fields ($B$ up to 30 T) shows that $\mu_{\text{exc}}$ increases rapidly until $x \sim 1.5\%$ and then oscillates around $\sim 0.08\ m_0$, $m_0$ being the electron mass in vacuum, up to about $x=6\%$. Surprisingly, for $x>8\%$ the exciton reduced mass decreases below the GaAs value, in agreement with the expectations of a $k\cdot p$ model. Such a behavior reveals the existence of different concentration intervals, where continuum states of the valence and conduction band hybridize with Bi-related levels at different extents, thus conferring to the band edges a localized or bandlike character for $x<6\%$ and $x>8\%$, respectively.

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I. INTRODUCTION

Recently, there has been much interest in the science and applications of highly mismatched semiconductor alloys. In these materials, the substitutional isovalent impurities have size and atomic potential largely different from those of the atoms being replaced. Quite often, these alloys exhibit uncommon compositional dependences of their fundamental band structure parameters (e.g., band-gap energy and carrier effective mass) thus boosting the number of opportunities for materials engineering. The unusual properties of highly mismatched semiconductors stem from the impuritylike localized character that the host band edges acquire as a consequence of the hybridization with the impurity wave function. Among other effects, this causes a largely nonlinear and unexpected variation of the band-gap energy with composition, as found in GaAs$_N^2$ and ZnTeS.$^3$ Within this class of nonconventional materials, GaAs$_{1-x}$Bi$_x$ has attracted much curiosity because of a series of interesting characteristics that include a large band gap reduction$^4-6$ and a giant spin-orbit bowing.$^7,8$ Despite the relevance of these effects for Terahertz$^9$ and telecom optoelectronics, solar cells, and spintronics, very little is known about the GaAs$_{1-x}$Bi$_x$ transport properties.$^{10,11}$ In particular, this applies to the carrier effective mass, which has a relevant applicative interest and can provide insightful information about nature and extent of the interaction between Bi-related levels and the conduction band (CB) and valence band (VB) states of the host crystal.

In this work, we find by magnetophotoluminescence measurements that the exciton reduced mass, $\mu_{\text{exc}}$, of GaAs$_{1-x}$Bi$_x$ shows an unexpected dependence on Bi concentration when it is measured in a wide concentration range ($x=0$–$10.6\%$). $\mu_{\text{exc}}$ first increases rapidly by 50% ($0 \leq x < 1.5\%$), then fluctuates around 0.08 $m_0$ ($1.5\% < x < 6\%$, $m_0$ being the electron mass in vacuum), eventually decreases below the GaAs value ($x>8\%$). Such behavior unveils a complex and unexpected evolution of the nature of the band edges. In the low Bi-concentration interval, the large value of the exciton reduced mass (about 0.08 $m_0$) indicates that the Bloch states of both the valence and conduction bands are affected on an equal footing as a consequence of Bi incorporation, although Refs. 10 and 11 report that the electron mobility is not affected largely by Bi incorporation. Instead, for $x>8\%$ we find that a conventional $k\cdot p$ behavior (i.e., a carrier mass decreasing with decreasing band-gap energy) is restored. This behavior has not been observed in the concentration range investigated in the better known alloy GaAs$_{1-x}$N$_x$. These results are discussed highlighting the role that the distribution of Bi atoms may play on the alloy band structure.

II. EXPERIMENT

The investigated GaAs$_{1-x}$Bi$_x$ samples have Bi concentration $x=0$, 0.6, 1.3, 1.7, 1.9, 3.0, 3.8, 4.5, 5.6, 8.5, and 10.6%. The samples were grown on (100) GaAs by solid source molecular beam epitaxy. Bi concentration was determined by combining x-ray diffraction and optical data. The growth conditions were set differently for different groups of samples to incorporate the wanted Bi content.$^{11,12}$ Table I reports the main growth parameters along with the relevant physical quantities determined in this work. All samples were characterized first by temperature- and power-dependent photoluminescence (PL) using a 532 nm laser for excitation and a 0.75 m monochrometer and an InGaAs linear array or Si charge coupled device detector (depending on sample emission energy) for spectral analysis. Magneto-PL was performed in a 30 T water-cooled resistive magnet, the luminescence being spectrally analyzed by a 0.32 m monochrometer and an InGaAs linear array or Si charge coupled device detector (depending on sample emission energy) for spectral analysis. Magneto-PL the optical path was purged of water vapor by nitrogen gas in order to make easier the determination of peak position, in particular for the $x=8.5\%$ and 10.6% samples. All spectra have been normalized by the system response.

III. RESULTS

At low temperature, $T$, and at almost any excitation power density, $P_{\text{exc}}$, PL spectra of disordered semiconductor alloys

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TABLE I. List of the samples investigated in this work. $x$ is the Bi concentration, determined by combining x-ray and optical data, $t$ is the GaAs$_{1-x}$Bi$_x$ layer thickness, $T_G$ is the GaAs$_{1-x}$Bi$_x$ layer growth temperature, FWHM is the full-width at half-maximum of the photoluminescence spectra recorded at 200 K under excitation power density $P_{\text{exc}} \sim 10$ W/cm$^2$, and $\mu_{\text{exc}}$ is the exciton reduced mass obtained by fitting the diamagnetic shift of the PL peak in the framework of an excitonic model ($m_0$ is the electron mass in vacuum).

<table>
<thead>
<tr>
<th>$x$ (%)</th>
<th>$t$ (nm)</th>
<th>$T_G$ (°C)</th>
<th>PL FWHM (meV)</th>
<th>$\mu_{\text{exc}}$ ($m_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>40</td>
<td>360</td>
<td>57 ± 8</td>
<td>0.062 ± 0.002</td>
</tr>
<tr>
<td>1.3</td>
<td>350</td>
<td>380</td>
<td>78 ± 5</td>
<td>0.082 ± 0.003</td>
</tr>
<tr>
<td>1.7</td>
<td>250</td>
<td>380</td>
<td>64 ± 3</td>
<td>0.072 ± 0.002</td>
</tr>
<tr>
<td>1.9</td>
<td>125</td>
<td>380</td>
<td>61 ± 3</td>
<td>0.079 ± 0.004</td>
</tr>
<tr>
<td>3.0</td>
<td>30</td>
<td>380</td>
<td>110 ± 8</td>
<td>0.080 ± 0.002</td>
</tr>
<tr>
<td>3.8</td>
<td>56</td>
<td>300</td>
<td>66 ± 3</td>
<td>0.071 ± 0.003</td>
</tr>
<tr>
<td>4.5</td>
<td>30</td>
<td>300</td>
<td>94 ± 10</td>
<td>0.082 ± 0.002</td>
</tr>
<tr>
<td>5.6</td>
<td>30</td>
<td>290</td>
<td>102 ± 4</td>
<td>0.078 ± 0.003</td>
</tr>
<tr>
<td>8.5</td>
<td>30</td>
<td>270</td>
<td>67 ± 3</td>
<td>0.050 ± 0.002</td>
</tr>
<tr>
<td>10.6</td>
<td>30</td>
<td>270</td>
<td>68 ± 3</td>
<td>0.046 ± 0.002</td>
</tr>
</tbody>
</table>

are dominated by the contribution of localized exciton (LE) states.\cite{13-20} Therefore, PL measurements vs $T$ and $P_{\text{exc}}$ have been performed for each sample in order to determine the experimental conditions that maximize the contribution of free-excitons (FE) and of band-to-band (B-B) recombination, which eventually dominates PL spectra at high $T$, with respect to that of localized states. Measurements at $T=10$ K and $\sim 200$ K are shown in Fig. 1 for two GaAs$_{1-x}$Bi$_x$ samples with $x=3.8\%$ [panels (a) and (b), respectively] and $8.5\%$ [panels (c) and (d), respectively]. In these as well as in all other samples, the low-$T$ PL spectra show a marked blue shift of the PL peak with increasing $P_{\text{exc}}$ and a low-energy skewed lineshape. These features are typical signatures of finite-density localized states.\cite{13-20} On the contrary, the PL peak energy of spectra taken at $T \sim 200$ K does not depend on $P_{\text{exc}}$ (but for a small blue shift due to band-filling effects) and the PL lineshapes are inhomogeneously and symmetrically broadened, that is typical of free excitons or of band-to-band transitions in disordered alloys. Consequently, magneto-photoluminescence measurements have been performed at relatively high power-density ($P_{\text{exc}} = 5-400$ W/cm$^2$) and temperature ($T \sim 200$ K).

Then, it is worth discussing the dependence on excitation power density of the diamagnetic shift $\Delta E_d(B)$. Figure 2 shows the shift of the PL peak energy with applied magnetic field $B$ in the $x=1.7\%$ sample for two excitation power densities differing by a factor 60. At lower power density and small fields, a quadratic behavior is observed thus indicating that excitons are involved in the transition considered. At higher power density, the creation of a rather large density of photogenerated carriers enhances the occurrence of carrier-carrier scattering events. In turn, this—along with likely carrier scattering from Bi clusters—disrupt the coherence of the electron/hole cyclotron orbit. Therefore, a diamagnetic shift begins to be observed at high $P_{\text{exc}}$ only at magnetic fields higher than a critical field $B_0$, as reported previously in degenerate GaAs and InN.\cite{21} It should also be noticed here that the dependence of $\Delta E_d$ on $B$ does not change with photogenerated carrier density once $B > B_0$. This warrants that the values of the carrier mass that can be derived by the $\Delta E_d$ vs $B$ dependence do not depend on $P_{\text{exc}}$ within the experimental uncertainty. In addition, this confirms a vanishing contribution of localized states to the PL spectra under the chosen experimental conditions. A situation similar to that shown in Fig. 2 has been observed in other samples too.

Panels (a) to (d) of Fig. 3 show the PL spectra of some of the GaAs$_{1-x}$Bi$_x$ samples recorded for different magnetic B ($T$) conditions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Peak-normalized photoluminescence (PL) spectra of two GaAs$_{1-x}$Bi$_x$ samples with different bismuth concentration [$x$ = 3.8\%: panels (a) and (b), and 8.5\%: panels (c) and (d)] recorded at different values of excitation power density for $T=10$ K and $T \sim 200$ K.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Free-exciton diamagnetic shift ($\Delta E_d$) as a function of magnetic field $B$ and different power densities for a GaAs$_{1-x}$Bi$_x$ sample with $x=1.7\%$. The typical error bar is shown for one point.}
\end{figure}
1.2 1.3 1.4
Energy (eV)

1.5
0.9 1.0 1.1 1.2
Energy (eV)

0.9 1.0
Energy (eV)

FIG. 3. Peak-normalized photoluminescence (PL) spectra of a selection of GaAs$_{1-x}$Bi$_x$ samples with different bismuth concentration [(a): $x=1.7\%$, (b): $x=5.6\%$, (c): $x=8.5\%$ and (d): $x=10.6\%$] recorded at different values of magnetic field ($B$ up to 30 T). Spectra of different samples were taken at $T=200$ K with a different value of the excitation power density (indicated in the figure).

fields at $T \sim 200$ K. All samples show a clear blue shift with magnetic field and a quite symmetrical broadening typical of disordered alloys. The dependence of the PL linewidth on $x$ is shown in Fig. 4 for spectra recorded at $T=200$ K under similar excitation power densities ($P_{\text{exc}} \sim 10$ W/cm$^2$); it cannot be accounted for by different growth conditions of the samples, at least on the ground of data reported in Table I.$^{12}$ We will further comment on the significance of these data in the Conclusions section.

An overview of the magneto-PL results is displayed in Fig. 5. The diamagnetic shift of GaAs$_{1-x}$Bi$_x$ (full symbols) is directly compared with the same quantity determined in GaAs (open symbols) under similar experimental conditions of $P_{\text{exc}}$ and $T$. The slope (and extent at fixed $B$) of $\Delta E_d(B)$ is roughly proportional to the inverse of the exciton reduced mass, $\mu_{\text{exc}}$. It is then evident at first glance that this slope displays a quite surprising behavior with increasing $B$: it rapidly decreases with respect to that of GaAs (for $x=0.6$ and 1.3%), then it remains roughly constant and well below that of GaAs (up to 5.6%), finally, it goes greater than that found in GaAs (for $x=8.5$ and 10.6%). The same figure shows also the analysis (lines) of the data by a numerical method$^{22-24}$ that applies to excitons under arbitrary magnetic fields. In this method, the exciton reduced mass and the zero-field energy are the only fitting parameters.$^{23}$ It could be questioned, however, whether FE or B-B transitions are involved in PL spectra taken at a temperature as high as $T=200$ K. As regards this question, magneto-PL measurements have been performed in a GaAs sample under the same experimental conditions of $P_{\text{exc}}$ and $T$ of the measurements done in GaAs$_{1-x}$Bi$_x$. The GaAs carrier masses are known and an

FIG. 4. Dependence on Bi concentration of the full-width at half-maximum (FWHM) of PL spectra recorded at 200 K under a same excitation power density ($P_{\text{exc}} \sim 10$ W/cm$^2$).


FIG. 5. (Color online) Free-exciton diamagnetic shift ($\Delta E_d$) as a function of magnetic field for GaAs$_{1-x}$Bi$_x$ samples (full symbols) with different bismuth concentration (indicated in the figure). Lines are fits to the data by means of the model reported in Refs. 22-24. The diamagnetic shift of GaAs bulk (recorded under similar experimental conditions) is displayed by open symbols. Notice the change of slope with respect to GaAs for $x=8.5$ and 10.6%.
analysis of the diamagnetic shift can be performed in terms of excitonic transitions, as for GaAs$_{1-x}$Bi$_x$ data, and of transitions between Landau levels of free electrons and holes. In the latter case, $\Delta E_d(B)$ should increase linearly with the applied field $B$ and the reduced masses, $\mu_{ll}$, would be directly proportional to the inverse of the slope of the diamagnetic shift. $\Delta E_d(B)$ values measured in GaAs and their theoretical fits in terms of both the excitonic and Landau level models are shown in Fig. 6. At a glance is clear that a linear fit poorly reproduces the experimental data in the whole magnetic field range. Moreover, the known value of the reduced electron and hole mass in GaAs ($\mu_{exc}=0.057 m_0$) (Ref. 25) is much nearer to the value we find in the excitonic model ($\mu_{exc}=0.058 \pm 0.002 m_0$, as derived by an average value over different measurements) than to the value found in the Landau level model ($\mu_{ll}=0.074 \pm 0.01 m_0$).26 In conclusion, present GaAs PL spectra seem to be dominated by free exciton recombination at $T \sim 200$ K. Similar conclusions have been previously obtained in GaAs by reflectivity measurements at room temperature27 and PL measurements28 (the latter measurements show that the PL peak position coincides with the FE peak energy even at room temperature).

As a final check, we have applied the Landau level model to the analysis of the diamagnetic shifts for $B > B_0$ in GaAs$_{1-x}$Bi$_x$ (linear fits to data are not shown in Fig. 5 for clarity purposes). Eventually, the best fit values of $\mu_{exc}$ (full black circles) and $\mu_{ll}$ (full gray diamonds) are shown as a function of Bi concentration in a double y-axis plot in Fig. 7. The $\mu_{exc}$ values are averages over similar mass values obtained for different temperatures and laser power densities (as long as the experimental conditions guarantee the absence of localized states), which has allowed an estimate of the experimental uncertainty shown in the figure. In agreement with the qualitative analysis of diamagnetic shift data in Fig. 5, $\mu_{exc}$ undergoes a rapid increase (from 0.058 $m_0$ for $x=0$ to 0.082 $m_0$ for $x=1.3\%$), then oscillates (around a mean value equal to 0.078 $\pm 0.005 m_0$), finally it decreases below the GaAs value (for $x>8\%$). The reduced masses $\mu_{ll}$, roughly 50% higher than $\mu_{exc}$, strictly mimic the dependence of $\mu_{exc}$ on Bi concentration. However, as found in the GaAs case, the diamagnetic shifts in Fig. 5 do not display a well defined linear dependence on $B$ even at the high magnetic fields $B > B_0$ required by the use of high excitation powers; see Fig. 2. In conclusion, all experimental evidences indicate that at $T \sim 200$ K the PL spectra are dominated by free exciton in GaAs as well as in GaAs$_{1-x}$Bi$_x$.

### IV. DISCUSSION

Since similar values of $\mu_{exc}$ are found in samples grown under different conditions (and sometimes even exhibiting sizably different PL linewidth; see, e.g., data for $x=1.9$, 3.0, and 4.5% samples reported in Table I), the dependence of $\mu_{exc}$ on Bi concentration is a genuine material feature, not related to the sample growth details. $\mu_{exc}$ values first indicate that the electron effective mass increases up to a value of 0.08 $m_0$, at least, in a wide Bi concentration range (1.3% $\leq x \leq 5.6\%$). Indeed, if the electron effective mass kept the value of 0.067 $m_0$ it has in GaAs, the reduced exciton mass $\mu_{exc}$ would never exceed that value, even in the limiting case that the hole effective mass $m_h$ got an infinite value upon Bi insertion in the GaAs lattice. On the contrary, in the whole range 1.3% $\leq x \leq 5.6\%$, $\mu_{exc}$ is equal to $\sim 0.08 m_0$ as already shown by us in the case of the $x=1.9\%$ sample.19,32 In turn, this greatly supports a strong effect of Bi insertion on the GaAs conduction band, independently of the choice of an excitonic or band-to-band recombination model. As a matter of fact, the value found for the electron effective mass in the Landau level model is higher by a factor $\sim 1.5$ than the value found in the excitonic model, even for an infinite hole effective mass.

This effect of Bi on the GaAs conduction band is unexpected and quite surprising on the ground of current theoretical models and experimental results.33 Phenomenological models34 and calculations based on the local density approximation7,35 find that Bi alloying of GaAs leads to the
formation of energy levels either resonant with\(^3\) or above\(^3\) the \textit{valence} band of the host. As the Bi concentration increases and the energy gap decreases, the band edges shift and cross the energy-pinned Bi-complex levels. In turn, this should give rise to sizable changes only of the \textit{hole} effective mass \(m_h\). These expectations are supported by the results reported for the dependence on N concentration of the free electron/exciton effective mass\(^3\) and localized exciton reduced mass\(^3\) in GaAs:N, a system somewhat similar to GaAs\(_{1-x}\)Bi\(_x\), once the roles of electron and holes (of conduction and valence bands) are exchanged. In GaAs:N, N introduces a level resonant with the conduction band, which only slightly affects the valence band states.\(^3\) On the ground of this similarity, therefore, no major change should be expected for the electron effective mass in GaAs\(_{1-x}\)Bi\(_x\), contrary to present results. It could be worth mentioning that recent structural measurements in samples similar to those studied here report on strong pairing and clustering of Bi atoms up to \(x=2.4\%\),\(^4\) also evidenced by low-temperature PL measurements.\(^2\) Bi pairs and clusters may then strongly affect the GaAs\(_{1-x}\)Bi\(_x\) electronic properties, as found\(^5\) in the case of N pairs in GaAs\(_{1-x}\)N\(_x\).

The inversion of the compositional dependence of \(\mu_{\text{exc}}\) for \(x>8\%\), namely, the remarkable decrease of the exciton reduced mass below the GaAs value, is even more intriguing. This “reversed” trend of \(\mu_{\text{exc}}\) would be expected for a “conventional” alloy, where the carrier effective mass decreases with the energy band gap \(E_g\). Indeed, for \(x>8\%\) the predictions of the \(k\cdot p\) model\(^2\) (open squares in Fig. 7) are in good agreement with the experimental values.\(^3\) Therefore, in this concentration range the localized character of the band extrema following Bi incorporation (and leading to an increase of \(\mu_{\text{exc}}\)) should lose importance with respect to the energy gap reduction, which causes, instead, a decrease of the carrier effective mass in a \(k\cdot p\) framework. We speculate that either the energy distance between the VB and CB edges and the Bi levels increases as to render negligible their interaction and/or the alloy recovers progressively a random atomic distribution of Bi for \(x>8\%\) (thus following more closely the expectations of a “regular” alloy). This latter hypothesis relates with recent theoretical calculations showing that in nitride semiconductors the band gap bowing\(^5\) and the carrier effective mass\(^4\) as well as electronic properties\(^5\) depend dramatically on details of disordered potential. Specifically, for a fixed N concentration in GaSb:N, the electron effective mass may increase or decrease with respect to that of N-free GaSb.\(^6\) Within this scenario, we point out the decrease of the PL full-width at half-maximum observed in the \(x=8.5\) and 10.6\% samples that suggests an increased alloy ordering consistent with the reduced mass data shown in Fig. 7.

\section*{V. CONCLUSIONS}

In summary, we investigated by magneto-PL the electronic properties of GaAs\(_{1-x}\)Bi\(_x\) alloys over a wide compositional range (\(x=0-10.6\%\)). The peculiar dependence of the exciton reduced mass on \(x\) reveals a rather fascinating evolution of the nature of the band extrema that change their character from impuritylike to bandlike. Indeed, depending on the Bi concentration we observe an exciton reduced mass greater (\(x<6\%\)) or smaller (\(x>8\%\)) than the same quantity measured in the Bi-free material. Moreover, conduction band states too are strongly affected by Bi incorporation, contrary to common expectations of an effect mainly restricted to the valence band states, only. These features should guide the theoretical modeling seemingly required to reformulate the electronic properties of GaAs\(_{1-x}\)Bi\(_x\). Finally, the decrease in the carrier effective mass we find for \(x>8\%\) turns out to be of particular interest in all those applications where carrier mobility is a relevant issue.

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26 Mass values and experimental uncertainties have been estimated by doing measurements under slightly different temperature and excitation power conditions.


31 We used for the electron mass $m_e \approx m_0 (1 + P^2/E_g)^{-1}$ and for the heavy hole mass $m_{hh} \approx m_0 (2Q^2/E' - 1)$, where $P^2 = 28.9$ eV, $Q^2 = 8$ eV, $E_g$ is the measured band gap energy and $E'$ is the energy distance between the top of the VB and $\Gamma_5$ states in the CB; see Refs. 29 and 30.

32 The different value found here for $x = 1.9\%$ with respect to that reported in Ref. 19 in the same sample is due to a more refined study involving measurements at different laser powers and temperatures.

33 At least at our knowledge, a very slight effect of Bi concentration on the conduction band has been reported only in the paper by B. Fluegel, A. Mascarenhas, A. J. Ptak, S. Tixier, E. C. Young, and T. Tiedje, Phys. Rev. B 76, 155209 (2007).


40 A slight effect of N concentration on the valence band has been reported in the paper by S. V. Dudiy, Alex Zunger, M. Felici, A. Polimeni, M. Capizzi, H. P. Xin, and C. W. Tu, Phys. Rev. B 74, 155303 (2006).


