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Influence of bismuth incorporation on the valence and conduction band edges of GaAs$_{1-x}$Bi$_x$

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We investigate the electronic properties of GaAs$_{1-x}$Bi$_x$ by photoluminescence at variable temperature ($T$=10–430 K) and high magnetic field ($B$=0–30 T). In GaAs$_{0.981}$Bi$_{0.019}$, localized state contribution to PL is dominant up to 150 K. At $T$=180 K the diamagnetic shift of the free-exciton states reveals a sizable increase in the carrier effective mass with respect to GaAs. Such an increase cannot be accounted for by an enhanced localized character of the valence band states, solely. Instead, it suggests that also the Bloch states of the conduction band are heavily affected by the presence of bismuth atoms. © 2008 American Institute of Physics. [DOI: 10.1063/1.2953176]

Recently, there has been great interest in the science and applications of isoelectronic doping of gallium arsenide. A thoroughly studied example is nitrogen-diluted GaAs$_{1-x}$N$_x$ ($x\sim 1\%$), where the large size and electronegativity mismatch between nitrogen and arsenic atoms leads to dramatic variations in the electronic properties of GaAs. These comprise a large decrease in the bandgap energy, $E_g$, an increase of the electron mass, and a gyromagnetic ratio, and a softened response of $E_g$ to external perturbations, such as hydrostatic pressure and temperature. A somewhat similar case is represented by the substitution of arsenic atoms with larger bismuth atoms in GaAs$_{1-x}$Bi$_x$. This alloy exhibits a sizable composition-induced shift of $E_g$ ($\sim 90$ meV/\% Bi) (Refs. 10–15) and a giant spin-orbit bowing ($80$ meV/\% Bi) (Refs. 14 and 15) that render GaAs$_{1-x}$Bi$_x$ of potential interest for long-wavelength emitters, photovoltaics, and spintronics. Despite several optical and structural studies and few transport measurements, nothing is known about the value of the carrier effective mass and controversial results have been reported on the thermal shift coefficient of the bandgap energy (regarded as an important characteristic for temperature-insensitive light emitters)

In this letter, we study by photoluminescence (PL) the electronic properties of a GaAs$_{1-x}$Bi$_x$ sample with a relatively large Bi concentration $x=1.9\%$. Temperature-dependent PL shows that carrier recombination is dominated by localized states up to $T=150$ K. From magneto-PL measurements performed at $T=180$ K in the $B=0–30$ T range we derive an exciton reduced mass, which exceeds by more than 60% the value measured in GaAs. This finding indicates that the states of both the valence and conduction band (CB) are affected by the strongly localized potential of Bi atoms.

The investigated sample is a 125 nm thick GaAs$_{0.981}$Bi$_{0.019}$ layer grown at 380 °C by molecular beam epitaxy on top of a 200 nm thick GaAs buffer layer. The thickness and composition of the Bi-containing layer were determined by x-ray diffraction patterns. The PL was excited by a frequency-doubled vanadate:Nd laser ($\lambda=532$ nm), spectrally analyzed by a 0.75 m long monochromator, and detected by a liquid-nitrogen-cooled InGaAs linear array detector. Magneto-PL was performed in a 30 T water-cooled resistive magnet, the luminescence being spectrally analyzed by a 0.75 m long monochromator, and detected by a liquid-nitrogen-cooled Si charge coupled device detector. All spectra have been normalized by the system response.

In semiconductor alloys, the unavoidable presence of local fluctuations around the crystal average composition gives rise to potential minima where carriers recombine preferentially at low temperature. This is also the case for GaAs$_{0.981}$Bi$_{0.019}$ whose PL spectra are shown in Fig. 1(a) for different temperatures. At $T=10$ K, the emission spectrum exhibits an asymmetric lineshape skewed to low energy due to localized states, as found in other materials. With increasing $T$, carriers trapped on potential minima are thermally ionized and recombination occurs prevalently from extended states, which start dominating PL for $T>150$ K. This is better evidenced in Figs. 1(b) and 1(c), where a power dependent study of PL is shown at $T=150$ K and 180 K, respectively. At $T=150$ K, localized states still contribute to PL, albeit at low density of photexcited carriers. These states can be hardly detected at $T=180$ K, where emission spectra are dominated by free-exciton recombination regardless of power density. Figure 1(d) shows the temperature-induced shift of the PL peak energy in GaAs$_{0.981}$Bi$_{0.019}$ and GaAs (the latter was derived from carrier recombination in the GaAs buffer layer) measured with respect to $T=10$ K. In the $300 \, K \leq T \leq 430 \, K$ interval, the data can be fitted by a linear dependence and the resulting thermal shift of the PL peak is $-0.46$ and $-0.36$ meV/K for $x=0\%$ and 1.9\%, respectively. These results are consistent with those reported in Ref. 11, where the thermal shift of bandgap energy, $\alpha_T$, was obtained by photoreflectance measurements ($\alpha_T=-0.23$ meV/K for $x=1.3\%$ and 1.50 K $\leq T \leq 300 \, K$).

In GaAs$_{1-x}$N$_x$, a reduced value of $\alpha_T$ upon N alloying was traced back to a sizable decrease in the $\Gamma$ character of the CB edge, because of a mixing between N localized states.
and N-perturbed CB states. On general grounds, it is expected that in GaAs larger Bi atoms introduce energy levels close to (or resonant with) the valence band (VB) states of the host lattice, thus leading to an increased localized character of the VB edge. We question this view on the basis of the exciton mass measurements presented in the following.

The carrier effective mass is a band structure parameter quite sensitive to the T character of the VB and/or CB edge of a semiconductor alloy. This parameter is usually derived from optical and transport experiments based on magnetic fields. Figures 2(a) and 2(b) show, respectively, the PL spectra of GaAs$_{0.981}$Bi$_{0.019}$ and GaAs for different values of magnetic field $B$ applied along the growth direction. The measurement temperature was set at 180 K as a tradeoff for minimizing the contribution of localized states on the low-energy side [see Figs. 1(b) and 1(c)] and of thermal broadening on the high-energy side of PL. At $B=30$ T, the free-exciton state in GaAs shifts by 22 meV. A much smaller shift (11 meV) is observed for GaAs$_{0.981}$Bi$_{0.019}$, instead. This points toward an increased value of the carrier masses in the Bi-containing material, as detailed below.

Figure 3 shows the diamagnetic shift $\Delta E_d$ of the free-exciton in GaAs (squares) and in GaAs$_{0.981}$Bi$_{0.019}$ (circles). The solid lines are best fits to the $\Delta E_d$ data by a numerical model$^6$—previously employed in GaAs$_{1-x}$N$_x$, see Ref. 6—where the exciton reduced mass $\mu_{\text{exc}}$ is the only fitting parameter. For GaAs we find $\mu_{\text{exc}}=0.054m_0$ (where $m_0$ is the electron mass in vacuum) in agreement with data reported in the literature. In GaAs$_{0.981}$Bi$_{0.019}$, the exciton reduced mass increases to $(0.088 \pm 0.003)m_0$. Quite interestingly, this $\mu_{\text{exc}}$ value is not conceivable under the hypothesis that the exciton mass increase is due entirely to the hole mass $m_h$ variation, as it could be assumed if Bi-related states interacted exclusively with the VB. Indeed, in the limit of a dispersionless VB and an unaffected CB (i.e., $m_h=\infty$ and $m_e=0.067m_0$, respectively) one should find $\mu_{\text{exc}}=0.067m_0$. In this case the diamagnetic shift dependence on $B$ would be that shown in Fig. 3 by the dashed line. Clearly, it cannot account for the experimental data of GaAs$_{0.981}$Bi$_{0.019}$. This suggests that the Bloch states of both the conduction and VB undergo an increased localized character upon Bi incorporation. This situation resembles to some extent the unexpected influence that N incorporation has on the VB of GaP$_{1-x}$N$_x$ with increasing N concentration. Therein, it was claimed and experimentally confirmed that a nitrogen-induced buildup of the L character near the VB edge is responsible for a surprising broad-absorption plateau observed between the $X_1$ and the $\Gamma_1$ critical points of GaP. In GaAs$_{1-x}$Bi$_x$, one can envisage that a qualitatively similar state mixing is induced by Bi, thus

![Figure 1](image1.png)

**FIG. 1.** (a) Peak-normalized PL spectra of GaAs$_{0.981}$Bi$_{0.019}$ for different temperatures. Laser power density $P_{\text{exc}}=33$ W/cm$^2$. (b) PL spectra at $T=150$ K for different laser power densities. LE and FE indicate localized carrier and free-exciton recombination, respectively. (c) Same as (b) for $T=180$ K. Notice the negligible contribution of LE to the PL spectra. (d) Temperature dependence of the shift of PL peak energy $\Delta E$ for GaAs$_{0.981}$Bi$_{0.019}$ (full diamonds) and GaAs (open squares) measured with respect to $T=10$ K. Lines are a guide to the eye.

![Figure 2](image2.png)

**FIG. 2.** (a) Peak-normalized PL spectra of GaAs$_{0.981}$Bi$_{0.019}$ in the free-exciton region at $T=180$ K for different magnetic field intensities. (b) Same as (a) for the GaAs excitonic recombination in the sample buffer layer.

![Figure 3](image3.png)

**FIG. 3.** Diamagnetic shift ($\Delta E_d$) as a function of magnetic field for GaAs$_{0.981}$Bi$_{0.019}$ (circles) and GaAs (squares). Gray solid lines are fits to the data by the numerical method reported in Ref. 6. The exciton reduced mass $\mu_{\text{exc}}$ is the only fitting parameter. The dashed line is the diamagnetic shift predicted on the basis of the model of Ref. 6 for $\mu_{\text{exc}}=0.067m_0$, namely, infinite hole mass and unperturbed electron mass. Clearly, such a limit cannot account for the GaAs$_{0.981}$Bi$_{0.019}$ data.
eventually resulting in a distortion of the CB structure, as well.

In conclusion, we performed PL in GaAs$_{1-x}$Bi$_x$ in an extended range of temperatures and magnetic field intensities. Temperature-dependent PL shows that (i) emission is dominated by localized excitons for $T \leq 150$ K; (ii) the PL peak energy reduces with $T$ at a rate slower than that observed in GaAs. These findings are consistent with a localization of carrier wavefunction around the Bi localized potential. From magnetic field-dependent PL we derived the GaAs$_{1-x}$Bi$_x$ exciton mass, whose value ($\mu_{\text{exc}}=0.088m_0$) implies necessarily an increase in the mass of both holes and electrons. Possibly, hybridization effects between Bi-related levels and the CB states determine the large value of the measured exciton mass. These data represent an important input to further theoretically and experimentally investigate the band structure of GaAs$_{1-x}$Bi$_x$.

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1For a review see Physics and Applications of Dilute Nitrides, edited by I. A. Buyanova and W. M. Chen (Taylor & Francis, New York, 2004), and Dilute Nitride Semiconductors, edited by M. Henini (Elsevier, Oxford UK, 2005).


