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$_{0.98}$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]
and N-perturbed CB states.\textsuperscript{22,23} 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, only.\textsuperscript{14,24,25} 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.\textsuperscript{3} This parameter is usually derived from optical\textsuperscript{3,6,26} and transport\textsuperscript{4} experiments based on magnetic fields. Figures 2(a) and 2(b) show, respectively, the PL spectra of GaAs\textsubscript{0.98}Bi\textsubscript{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\textsubscript{0.98}Bi\textsubscript{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\textsubscript{0.98}Bi\textsubscript{0.019} (circles). The solid lines are best fits to the \(\Delta E_d\) data by a numerical model\textsuperscript{27}—previously employed in GaAs\textsubscript{1-x}N\textsubscript{x}, see Ref. 6—where the exciton reduced mass \(\mu_{\text{exc}}\) is the only fitting parameter. For GaAs we find \(\mu_{\text{exc}} = 0.054 m_0\) (\(m_0\) is the electron mass in vacuum) in agreement with data reported in the literature.\textsuperscript{28} In GaAs\textsubscript{0.98}Bi\textsubscript{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,

\[\mu_{\text{exc}} \propto \frac{1}{m_h}.\]

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., \(m_h \to \infty\) and \(m_e = 0.067 m_0\), respectively) one should find \(\mu_{\text{exc}} = 0.067 m_0\). 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\textsubscript{0.98}Bi\textsubscript{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\textsubscript{1-x}N\textsubscript{x} with increasing N concentration.\textsuperscript{29} 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\textsubscript{1-x}Bi\textsubscript{x}, one can envisage that a qualitatively similar state mixing is induced by Bi, thus

\[\mu_{\text{exc}} \approx \frac{\mu_{\text{exc}} - \mu_{\text{exc}}^0}{1 - \alpha (N_{\text{Bi}}/N_{\text{Ga}})}\]

FIG. 1. (a) Peak-normalized PL spectra of GaAs\textsubscript{0.98}Bi\textsubscript{0.019} for different temperatures. Laser power density \(P_{\text{exc}} = 33\) W/cm\textsuperscript{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\textsubscript{0.98}Bi\textsubscript{0.019} (full diamonds) and GaAs (open squares) measured with respect to \(T = 10\) K. Lines are a guide to the eye.

FIG. 2. (a) Peak-normalized PL spectra of GaAs\textsubscript{0.98}Bi\textsubscript{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.

FIG. 3. Diamagnetic shift (\(\Delta E_d\)) as a function of magnetic field for GaAs\textsubscript{0.98}Bi\textsubscript{0.019} (circles) and GaAs (squares). Gray solid lines are fits to the data by the numerical method reported in Ref. 27. 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. 27 for \(\mu_{\text{exc}} = 0.067 m_0\), namely, infinite hole mass and unperturbed electron mass. Clearly, such a limit cannot account for the GaAs\textsubscript{0.98}Bi\textsubscript{0.019} data.
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 ($\mu_{exc} = 0.088m_0$) implies necessarily an increase in the mass of both holes and electrons. Possibly, hybridization effects between Bi-related states 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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1 For 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).