Comparison of the dilute bismide and nitride alloys GaAsBi and GaAsN

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1 Introduction

Recently there has been a surge of interest in a new family of III–V semiconductor alloys termed dilute bismides. Analogous to the dilute nitride alloys, GaAs$_{1-x}$Bi$_x$ and GaP$_x$N$_{1-x}$, the dilute bismides also exhibit a giant bandgap reduction, albeit with subtle differences [1]. In the case of GaAs$_{1-x}$Bi$_x$, the conduction band transport is predicted to be much less perturbed than in GaAs$_{1-x}$N$_x$ where the degradation in electron transport that proved to be detrimental for applications of the dilute nitrides in multijunction solar cells and VCSEL laser technologies. A common feature in both these alloy systems is that nitrogen and bismuth behave as isoelectronic traps in the host semiconductor, e.g. in GaAs and GaP, N and Bi behave as electron traps and hole traps respectively. Although in both GaAs and GaP the incorporation of N results in a large redshift of the absorption edge, the primary contributors to the absorption in the new band edge are in fact very different for these alloys [2], being hostlike states for GaAs but N impurity like states in GaP, due to the fact that an isolated N impurity does not produce a bound state in GaAs but does so in GaP. Towards the impurity limit of the dilute alloy, it is well known that in GaP, an isolated N or Bi impurity introduces a bound state below the conduction band minimum (CBM) or above the valence band maximum (VBM) [3, 4] and, that in GaAs, the isolated N impurity state is resonant above the CBM [5]. However, the location of the Bi impurity state in GaAs is unknown experimentally, although a bound state was predicted at 180 meV above the VBM in the dilute limit, and thus the VBM of the GaAs$_{1-x}$Bi$_x$ alloy was suggested to derive from the Bi impurity state, based on a first-principles density function theory calculation using relatively small supercells [6]. The existence of such a deep bound state would be rather surprising, given the fact that the Bi bound state lies only ~60 meV above the VBM in GaP, which in fact makes it more favorable for Bi to have a bound state. Our calculation, using a self-consistent pseudopotential-based charge patching method and large supercells with up to 4096 atoms, finds that the alloy VBM is derived from the host VBM rather than the Bi bound state, that Bi forms a resonant state below the VBM rather than a bound state, and that the isolated Bi impurity state has a larger pressure coefficient (in magnitude) than the band gap [1]. The prediction is that $E_{\text{Bi}}$ extrapolates to ~80 meV below the VBM of GaAs in the dilute doping limit (i.e., the supercell size $n \to \infty$) and that the bandgap volume deformation potential for $E_{\text{g}}$ is larger than that of $E_{\text{Bi}}$ (e.g., −8.03 eV vs. −7.81 eV for $x \to 0$ and −8.75 eV vs. −7.84 eV for $x = 3.125\%$), implying that applying a hydrostatic pressure will not make $E_{\text{Bi}}$ emerge from the VB, in stark contrast to the behavior of the N impurity state that drops into the band gap under pressure [5]. The expected pressure behavior of $E_{\text{Bi}}$ is in-
deed consistent with a recent experimental finding that Te (an isoelectronic donor) bound state in ZnS:Te has a larger pressure coefficient than that of the band gap [7].

2 Theory The bandgap volume deformation potential $\alpha = \alpha_{CBM}^{VBM} - \alpha_{VBM}^{CBM}$, where $\alpha_{CBM}^{VBM}$ and $\alpha_{VBM}^{CBM}$ are the volume deformation potential for the conduction band and valence band, respectively. Typically $\alpha_{CBM}^{VBM} < 0$ and $|\alpha_{CBM}^{VBM}| > |\alpha_{VBM}^{CBM}|$. If $\alpha_{VBM}^{CBM} < 0$, as was implicitly assumed in our original paper [1] by accepting a previously calculated result (e.g., $\alpha_{VBM}^{CBM} = -1.21$ eV) [8], the calculated bandgap deformation potentials would imply that the Bi impurity state had a smaller absolute deformation potential (in magnitude), i.e., $|\alpha_{VBM}^{CBM}| < |\alpha_{CBM}^{VBM}|$. However, a very recent theoretical study has indicated that $\alpha_{VBM}^{CBM} > 0$ for most semiconductors (e.g., $\alpha_{VBM}^{CBM} = +2.24$ eV) [9]. Based on this new understanding, one can conclude that the Bi impurity state has a larger absolute deformation potential, i.e., $\alpha_{VBM}^{CBM} > \alpha_{VBM}^{CBM}$.

Another interesting contrast between GaAs$_{1-x}$Bi, and GaAs$_{1-x}$N$_x$ is the dependence of the valence band spin-orbit interaction on the doping level. For the GaAs$_{1-x}$Bi$_x$ alloy, it has been found that this dependence is extremely weak [10], whereas for GaAs$_{1-x}$Bi$_x$, the spin–orbit interaction is expected to be enhanced strongly with Bi incorporation [11], and has been confirmed experimentally [11]. Such a contrast is due to the fact that the hole state is strongly localized on the Bi site and anti-localized from the N site, which leads to the disproportional change of the spin–orbit interaction when either of the impurities is introduced into the host.

Although for both GaP:N and GaAs:N, the existence of bound exciton states associated with paired nitrogen centers (NN’s) is well documented in the Refs. [3, 12], impurity states associated with paired Bi centers in III–V semiconductors have not been unambiguously identified. Despite a recent suggestion that small Bi clusters might be present in GaAs$_{1-x}$Bi$_x$ [13] we would like to point out another significant disparity between N and Bi impurities in III–V semiconductors, that is, one being much smaller and the other much larger than the host atom. Therefore, it could be energetically less favorable for Bi to cluster than for N.

A better understanding of the behavior of Bi as an impurity in III–V semiconductors and the evolution of the electronic structure of III–V–Bi with increasing Bi doping level is critically needed for further exploring its potential for device applications.

3 Experimental approach GaAs$_{1-x}$Bi$_x$ epilayers of thickness ~0.3 µm were grown on (100) oriented GaAs substrates. The Bi concentration in the samples was measured using secondary ion mass spectroscopy (SIMS) and was estimated to be less than ~2 x 10$^{19}$ cm$^{-3}$. The samples also contained some unintentional donors/acceptors. The photoluminescence (PL) measurements were performed with the samples in cold Helium gas in a pumped cryostat. The PL emission was dispersed by a 0.64 m spectrometer and detected by a cooled CCD. The above gap excitation was provided by a Nd laser at 532 nm.

Figure 1 (online colour at: www.pss-b.com) PL spectra of a GaAs$_{1-x}$Bi$_x$ sample ($x = 0.045\%$) near the GaAs band gap region at different temperatures. The intensity of the g-line (~1.51 eV) decreases exponentially with increasing temperature. All the curves have been normalized to the free exciton-polariton peak at 1.515 eV and shifted vertically for clarity.

4 Photoluminescence studies Figure 1 shows the PL spectra of a GaAs$_{1-x}$Bi$_x$ sample ($x = 0.045\%$) at different temperatures. The sharp line at 1.51 eV is called the g-line and the line shape of the g-line with its low energy shoulder extending up to ~2 meV is quite similar to the shape of the g-line observed in undoped GaAs, GaAs doped with Be, Ge and Si [14] and GaAs implanted with Ca$^+$ ions [15]. The intensity of the g-line decreases very rapidly with increasing temperatures. In the range 10–20 K this decrease is approximately exponential, with an activation energy of 4.6 meV and agrees very well with the reported values [16, 17]. The time constant obtained (~1 ns) from the time resolved PL measurements of the g-line also agrees well with the values found in the Ref. [18]. It has been suggested that g-line was associated with a neutral acceptor-complex-defect bound exciton involving the major residual carbon acceptor and an isoelectronic defect [19] or a two-acceptor–one-donor complex [17].

Several undulations were observed in the 20 meV range immediately below g-line. If the undulations were due to different Bi–Bi pairs, then, each Bi–Bi pair line would have a multiplet structure and one would expect to see thermalization between the multiplets and thus a shift...
perturbation to the GaAs band structure, where it was observed that the band edge excitonic absorption peak as well as PL peaks due to the decay of excitons bound to nitrogen pairs showed a red shift with increasing N concentration [23]. Another important point is that we did not observe any emission related to the decay of bound excitons associated with isolated Bi and Bi–Bi pairs, which is consistent with the theoretical prediction that the isolated Bi state is resonant within the valence band [1, 22] and that Bi does not form pair states in the forbidden band gap. These results corroborate earlier experimental studies that failed to observe Bi–Bi pairs in GaP:Bi [24, 25].

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5 Conclusions

We studied several GaAs<sub>x</sub>Bi samples with very dilute concentrations (x < 0.045%) of Bi and observed PL spectra characteristically similar to that shown in Figs. 1 and 2. The g-line and the undulatory peaks show a red shift with increasing Bi concentration due to the decrease in band gap as a result of Bi induced perturbation to the host band structure. It is important to note that the Bi induced perturbation to the GaAs band structure is very strong and a small amount of Bi, even less than 0.045% can perturb the host band structure sufficiently enough to give rise to the readily observable redshift. This is similar to the case of the nitrogen induced shift. This is similar to the case of the nitrogen induced

in the peak position. In the case of N–N pairs [20] and donor–acceptor pairs [21] a complete thermalization between the multiplets is seen. As shown in Fig. 2, no such thermalization was observed. As the temperature is increased, the shape and position of the undulation peaks remain unchanged, but the high-energy undulations are quenched first. Furthermore, if the undulations were associated with different Bi–Bi pairs, their energy separations would be too small compared to an early theoretical calculation [22]. These considerations enable us to discount the possibility that undulations are due to different Bi–Bi pairs. At this point, the origin of these lines is unclear and further experimental studies are in progress.

Figure 2 (online colour at: www.pss-b.com) Undulatory spectra below the g-line at different temperature for GaAs<sub>x</sub>Bi sample (x = 0.045%). As the temperature is increased, the shape and position of the undulation peaks remain unchanged, but the high-energy undulations are quenched first.

Note that the Bi induced perturbation to the GaAs band structure, where it was observed that the band edge excitonic absorption peak as well as PL peaks due to the decay of excitons bound to nitrogen pairs showed a red shift with increasing N concentration [23]. Another important point is that we did not observe any emission related to the decay of bound excitons associated with isolated Bi and Bi–Bi pairs, which is consistent with the theoretical prediction that the isolated Bi state is resonant within the valence band [1, 22] and that Bi does not form pair states in the forbidden band gap. These results corroborate earlier experimental studies that failed to observe Bi–Bi pairs in GaP:Bi [24, 25].

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