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The effect of Bi composition to the optical quality of GaAs_{1-x}Bi_x

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GaAs_{1-x}Bi_x alloys grown by molecular beam epitaxy for x up to 0.06 were studied by photoluminescence (PL). The results indicate that dilute fractions of bismuth (Bi) with $x < 0.025$ improve the material quality of this low temperature growth alloys by reducing the density of gallium (Ga) and/or arsenic related defects. The crystal quality starts to degrade at higher Bi concentration probably due to significant amount of Bi-related defects, Bi_{Ga}. However, the room temperature PL intensity continues to increase with Bi content for the range studied due to greater band-gap offset between GaAs and GaAs_{1-x}Bi_x. Analysis carried out shows no correlation between localization effects and the room temperature PL enhancement. © 2011 American Institute of Physics. [doi:10.1063/1.3617461]

Recently, bismuth (Bi) containing semiconductors have attracted increasing interest due to the large band gap reduction of ~ 88 meV/% Bi for GaAs_{1-x}Bi_x, relatively temperature insensitive band gap and large spin-orbit splitting.¹⁻³ Hence, such alloys are promising for long wavelength optoelectronic devices and spintronic applications. Furthermore, the incorporation of nitrogen to form quaternary GaNAsBi allows lattice matching to GaAs substrates and further band gap reduction. The crystal quality of III-V alloys is highly affected by the growth temperature. A low growth temperature is undesirable as it typically leads to the increase of defect densities and optical quality degradation. However, for the growth of Bi containing alloys, a low growth temperature typically between 270 °C and 400 °C is required to avoid Bi segregation during growth thereby incorporating significant amounts of Bi.³⁻⁶

It has been reported that increasing Bi fractions of up to $x = 0.045$ leads to an improvement of the optical quality of GaAs_{1-x}Bi_x.⁷ Enhanced photoluminescence (PL) in GaAs_{1-x}Bi_x is highly desirable as it may lead to reduced threshold current densities for laser diodes. It was also suggested that the composition dependent PL enhancement was due to localization effects induced by Bi incorporation similar to the role of indium in wide-gap InGaN and InAlGaN alloys.^{7,8} This is in contrast to N alloying in GaAs which degrades the optical quality and where localization is associated with defects. However, this result is in contrast with Ref. 9 which observed a decreasing PL intensity with Bi content for x up to 0.026, in metal-organic vapour phase epitaxy grown samples. To date, the composition dependent PL of GaAs_{1-x}Bi_x has not been verified, and the origin of PL intensity enhancement is still not well understood. In this letter, we report a detailed PL study on the effect of Bi concentra-

tion to the optical quality of GaAs_{1-x}Bi_x (x up to 0.06). The reason for PL intensity enhancement also will be addressed.

The samples used in this study were grown using an Omicron molecular beam epitaxy—scanning tunneling microscopy (MBE-STM) system. The semi-insulating GaAs (100) substrate used was cleaved into 11.0×3.5 mm² pieces to fit into the substrate holder. The cleaning and oxide removal procedures were as described in Ref. 10. A 80 nm GaAs buffer was grown at 590 °C, followed by GaAs_{1-x}Bi_x layer at a rate of 160 nm per hour and then capped with 50 nm of GaAs. Table I summarized the GaAs_{1-x}Bi_x samples studied in this work. The (004) high resolution x-ray diffraction (HRXRD) $\theta/2\theta$ scans of the as-grown samples were measured. The epilayer thicknesses and Bi composition were determined by fitting the HRXRD scans using RADS Mercury software, assuming a GaBi lattice constant of 6.324 Å.¹¹ For the PL measurements, the sample was excited with a continuous-wave 532 nm wavelength diode-pumped solid state laser. The PL was dispersed using a monochromator and then detected by a liquid nitrogen-cooled germanium detector. A phase-sensitive detection technique was implemented using a lock-in amplifier and a chopper. The spectral response of the PL system (Ge detector, monochromator grating, and associated optics) was determined using a calibrated white light reference source and used to correct the measured PL data.

Figure 1(a) shows the normalized PL data of Set C samples measured at room temperature. The incorporation of Bi

TABLE I. Summary of samples studied in this work.

Sample set	Number of samples	GaAsBi thickness (nm)	GaAsBi growth temperature (°C)
A	3	100	420
B	3	50	400
C	4	25	400

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FIG. 1. (a) Normalised room temperature PL spectra for Set C samples (b) PL intensity versus Bi content at room temperature with $P_e = 320 \text{ Wcm}^{-2}$.

reduces the band gap of GaAs and the highest Bi content sample, GaAs_{0.94}Bi_{0.06} has a peak wavelength of $1.2 \mu\text{m}$. The band gap reduction is mainly due to the increase of valence band maximum due to the valence band anti-crossing interaction.¹² However, the full-width-at-half-maximum (FWHM) lies between 74 and 84 meV, which is significantly larger than the FWHM of GaAs (26 meV). Figure 1(b) shows the PL intensity comparison as a function of Bi content with excitation power, $P_e = 320 \text{ Wcm}^{-2}$. The PL intensity of GaAs_{0.94}Bi_{0.06} sample is approximately 100 times greater than the thicker GaAs_{0.995}Bi_{0.005} sample. Interestingly, the PL intensity of GaAs_{0.94}Bi_{0.06} is also twice compared to the PL intensity of a high quality $3 \mu\text{m}$ thick GaAs reference sample (grown by standard V90 MBE at 580°C). Even though the GaAs sample is a different structure, the comparison still gives useful information about the crystal quality of the GaAs_{1-x}Bi_x samples. The PL intensity increases rapidly at low Bi content but starts to saturate at high Bi composition. The composition dependent PL enhancement may be due to (i) higher Bi content reduces the defect density, (ii) greater carrier confinement due to larger GaAs/GaAsBi band offset for high Bi content samples, or (iii) higher Bi content increases the localisation effects near the valence band maximum, efficiently trapping holes and making excitons less sensitive to non-radiative recombination centers.

In order to verify the presence of localization effects in the samples, temperature dependent PL measurements were carried out. The measurements used $P_e = 53 \text{ Wcm}^{-2}$, power density that avoids saturating the localized states while ensuring measurable PL signals from all samples at room temperature. The data of PL peak energy against temperature for Set C samples are shown in Figure 2(a). All samples

FIG. 2. (a) Temperature dependent of PL peak energy of Set C samples and (b) FWHM measured at 10 K when excited with $P_e = 53 \text{ Wcm}^{-2}$. The dashed lines are fitting using Varshni equation.

showed the S-shape behavior which is a well-known signature of localization effects. However, the localization energy varies from sample to sample. The data were fitted using the Varshni equation,¹³

$$E_g(T) = E_o - \alpha T^2 / (T + \beta), \quad (1)$$

where E_o is the 0 K band gap and α and β are fitting parameters and these are summarized in Table II. The localization energy for a particular temperature is defined as $E_{loc}(T) = E_g(T) - E_{PL}(T)$.¹⁴ The value of the maximum localization energy, E_{maxloc} , is also included in Table II. As x increases from 0.022 to 0.033, E_{maxloc} initially increases from 51 to 90 meV and then decreases to 46 and 36 meV for $x = 0.048$ and 0.06 , respectively. From Figure 2(b), the 10 K FWHM of Set C samples also shows a maximum at $x = 0.033$, consistent with the trend observed for E_{maxloc} . This observation is expected as the 10 K linewidth is mainly affected by alloy fluctuations and Bi clustering, thus indicative of the relative localization strength. However, for Set A and B samples, the linewidth is approximately constant with an average value of 77 meV. This means that the localization energy is unchanged for both sets of samples. Data in

TABLE II. Varshni fitting parameters and E_{maxloc} for Set C samples.

Bi content	E_{maxloc} (meV)	E_o (eV)	α (meV/K)	β (K)
0.022	51	1.333	0.45	250
0.033	90	1.244	0.37	280
0.048	46	1.165	0.37	280
0.060	36	1.097	0.39	260

FIG. 3. PL intensity measured at 10 K with $P_e = 53 \text{ W cm}^{-2}$.

Figure 2 do not show an increase in localization energy and FWHM with increasing x for the range studied. Hence, localization effects are unlikely to be the main mechanism for the increased PL shown in Figure 1(b).

Figure 3 shows the 10 K PL intensity plotted as a function of Bi concentration. For Set A samples, the PL intensity increases with increasing Bi content but decreases for Sets B and C. The results are in contrast with the room temperature PL intensity trend observed in Figure 1(b). The results suggest that the incorporation of Bi in GaAs of up to ~ 0.025 improves the material quality. It is well known that growing GaAs at significantly lower than the optimal growth temperature (580°C) induces many defects such as As-related defects (As-interstitial¹⁵ and As-antisite, As_{Ga} ¹⁶) and Ga vacancies.¹⁷ Incorporating Bi during low temperature growth enhances surface migration, thus reducing the density of Ga and/or As-related defects.¹⁸ Based on deep level transient spectroscopy (DLTS) study reported recently, the trap concentrations in $\text{GaAs}_{0.988}\text{Bi}_{0.012}$ is ~ 10 times lower than GaAs, when both are grown at 370°C .¹⁸ However, Bi incorporation also introduces Bi-related defects such as Bi-antisite, Bi_{Ga} .¹⁹ For $x > 0.025$, the Bi-related defects started to become significant, thus degrade the optical quality of $\text{GaAs}_{1-x}\text{Bi}_x$. This explains the PL intensity reduction for set B and C measured at 10 K.

The room temperature PL intensity enhancement observed in Figure 1(b) is the result of more efficient carrier confinement (and higher quality for $x < 0.025$) due to a larger band gap offset (between GaAs and $\text{GaAs}_{1-x}\text{Bi}_x$) with increasing Bi content. The PL enhancement slowly saturates when the valence band offset becomes large enough to avoid carrier escape. It is expected that the room temperature PL intensity will start to decrease for $x > 0.06$ due to material quality degradation. In Ref. 7, the room temperature PL intensity increases only up to 0.045 (in this work up to 0.06) probably due to higher density of Bi-related defects as a result of lower growth temperature ($270 - 300^\circ\text{C}$). It is important to note that even though the crystal quality gradually

degrades for $x > 0.025$, the PL intensity of $\text{GaAs}_{0.94}\text{Bi}_{0.06}$ (at room temperature and 10 K) is still comparable to the PL intensity of the high quality GaAs reference sample.

In summary, for $\text{GaAs}_{1-x}\text{Bi}_x$ samples grown by MBE, the optical quality is highly dependent on the Bi concentration. The incorporation of Bi in GaAs reduces the density of Ga and/or As-related defects as well as introducing Bi-related defects. For dilute amount of Bi ($x < 0.025$), the crystal quality improves but further increase of Bi causes degradation to the material quality probably due to significant amount of Bi-related defects. However, the room temperature PL continues to increase up to $x = 0.06$ due to greater band-gap offset between GaAs and $\text{GaAs}_{1-x}\text{Bi}_x$ layer. No clear correlation was found that relates the localization effect to the room temperature PL intensity enhancement.

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