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Effects of rapid thermal annealing on GaAs_{1-x}Bi_x alloys

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The effects of rapid thermal annealing on the optical and structural properties of GaAs_{1-x}Bi_x alloys for x ranging from 0.022 to 0.065 were investigated. At room temperature, the annealed GaAs_{1-x}Bi_x showed modest improvement (~ 3 times) in photoluminescence (PL) while the PL peak wavelength remained relatively unchanged. It was found that bismuth related defects are not easily removed by annealing and the PL improvement may be dominated by the reduction of other types of defects including arsenic and gallium related defects. Also, the optimum annealing temperature is Bi composition dependent. For samples with $x < 0.048$, the optimum annealing temperature is 700 °C but reduces to 600 °C for higher compositions. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4731784>]

The incorporation of bismuth (Bi) in GaAs introduces many interesting properties including large band gap reduction, large spin-orbit splitting, and a relatively temperature insensitive band gap.¹⁻³ Hence, increasing interest has been shown towards this material system for long wavelength optoelectronic applications. However, the growth of GaAs_{1-x}Bi_x poses several challenges. The Bi flux has to be accurately controlled as excess Bi during growth may accumulate and form Bi droplets, while insufficient Bi flux may cause surface roughening due to low surfactant effects.⁴⁻⁶ A low growth temperature (270–400 °C) is also required in order to incorporate a significant fraction of Bi in GaAs to extend the emission wavelength.^{4,7}

Room temperature photoluminescence (PL) of GaAs_{1-x}Bi_x on GaAs with PL peak emission of up to 1.2 μm has been reported previously.⁷ Since the samples were grown at relatively low temperature, wafer quality might be expected to improve by thermal annealing as in the case for GaNAs samples.⁸ However, Feng *et al.* reported that annealing GaAs_{1-x}Bi_x ($x = 0.032$) grown by molecular beam epitaxy (MBE) at up to 800 °C did not improve its room temperature PL.⁹ The PL peak wavelength also blue-shifted by 8 meV which was attributed to the micro-scale changes inside the epilayer rather than Bi out diffusion.⁹ For metal-organic vapor phase epitaxy (MOVPE) grown GaAs_{1-x}Bi_x, PL intensity improvement of more than 10 times and full-width-at-half-maximum (FWHM) reduction of 23 meV were observed at 10 K.¹⁰ Despite the significant improvements in Ref. 10, no PL emission could be detected above 100 K. Recently, photo-reflectance measurement performed by Chine *et al.* shows that the band gap of GaAs_{1-x}Bi_x was red-shifted by 60 meV after annealing at 600 °C.¹¹

The mixed results in the literature shows that the effects of annealing on GaAs_{1-x}Bi_x alloys are not well understood.

In this letter, a systematic study on the effects of annealing on the optical and structural properties of MBE grown GaAs_{1-x}Bi_x alloys will be reported. This study uses samples with Bi content between 0.022 and 0.065. The origin of the optical quality improvement will also be discussed.

The samples used in this study were grown using an Omicron molecular beam epitaxy-scanning tunneling microscopy (MBE-STM) system. The samples were grown on pieces cleaved from semi-insulating GaAs (100) substrates. Each sample consists of a GaAs buffer, 10–50 nm GaAs_{1-x}Bi_x epilayer, and a GaAs cap. This work uses seven samples in total; one GaAs reference sample and six GaAs_{1-x}Bi_x samples. All samples were grown at 400 °C (including GaAs reference) except for samples with $x = 0.04$ and 0.065 which were grown at 420 and 380 °C, respectively. The sample size is either 11.0 $\times$ 3.5 mm² or 11.5 $\times$ 12.0 mm² depending on the substrate holder used during growth. Each sample was then cleaved into pieces with an average size of 5.7 $\times$ 4.8 mm², large enough to avoid edge effects in subsequent PL measurements. Post-growth annealing was carried out in a rapid thermal annealing (RTA) system in nitrogen ambient. In order to prevent arsenic decomposition during annealing, the samples were proximity-capped with a GaAs substrate. Samples were annealed at 600, 700, and 800 °C while the annealing duration was fixed at 30 s.

For PL measurements, the samples were excited with a continuous-wave 532 nm wavelength laser. The PL was dispersed by a monochromator and was detected by a liquid nitrogen-cooled germanium detector. (004) high resolution x-ray diffraction (HR-XRD) $\omega/2\theta$ scans were carried out to determine the Bi composition and to evaluate the structural properties of the samples.

Figure 1 shows the room temperature PL data of as-grown and annealed GaAs_{1-x}Bi_x with $x = 0.04$. For annealing temperatures of 600 and 700 °C, the PL intensity increases (compared to the as-grown) while the PL peak wavelength remained relatively unchanged. This result is encouraging as optical quality improvement could be obtained without

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FIG. 1. PL data of as-grown and annealed GaAsBi with Bi content of 0.04 measured at room temperature.

compromising the PL peak wavelength. However, the optical quality degraded significantly and the PL peak wavelength blue-shifted by 4 meV when annealed at 800 °C. Hence, 700 °C is the optimum annealing temperature with ~ 3 times of PL intensity improvement. The improvement factor is small compared to the effect of annealing on other semiconductor alloys (i.e., GaAs and GaNAs). The integrated PL intensity of the GaAs reference sample (grown at 400 °C) increases by ~ 6 times when annealed at 700 °C. This shows that the arsenic (As) and gallium (Ga) related defects generated by low growth temperature are easily removed by thermal annealing. In the case of GaNAs, annealing typically leads to significant PL improvement (~ 10 times) but at the expense of PL peak wavelength blue-shift. The significant PL improvement is mainly attributed to the removal of high density of nitrogen interstitials.⁸

The optimum annealing temperature (700 °C) shown in Figure 1 was then used to anneal other GaAs_{1-x}Bi_x samples. The room temperature PL measurements of the as-grown and annealed samples were then carried out. For a given Bi content, the integrated PL improvement ratio between the annealed and as-grown samples was obtained. The PL improvement ratio versus Bi content is shown in Figure 2(a). For samples with $x < 0.048$, PL improvement of ~ 3 times was observed. However, the level of PL improvement reduced for higher Bi content samples and in fact degraded the luminescence of the sample with $x = 0.065$.

In order to investigate the diminishing improvement in PL intensity for high Bi content samples in Figure 2(a), pieces from GaAs_{1-x}Bi_x sample with $x = 0.065$ were annealed at different temperatures and the integrated PL improvement ratio is shown in Figure 2(b). It is found that the optimum annealing temperature for GaAs_{0.935}Bi_{0.065} sample is 600 °C, (100 °C lower than that of the GaAs_{0.96}Bi_{0.04} sample), suggesting that the optimum annealing temperature is dependent on Bi composition. Hence, using a fixed annealing temperature of 700 °C for all samples ($x = 0.022$ to 0.065) will give rise to different PL improvement ratio, resulting in the trend in Figure 2(a). Composition dependent of optimum annealing temperatures has been observed in other material systems. It was reported that the optimum annealing temperature of GaNAs reduces from 1000 to 700 °C when the N content increases from 0.06% to 6%.^{12,13}

FIG. 2. (a) The PL improvement ratio of annealed samples with different Bi content. The samples were annealed at 700 °C for 30 s (b) The PL improvement ratio against annealing temperatures for GaAsBi pieces with $x = 0.04$ and 0.065

The HR-XRD data for the GaAs_{0.935}Bi_{0.065} sample are compared in Figure 3. Annealing at 600 °C causes no noticeable structural change compared to the as-grown piece and the average Bi content remained the same. However, the peak-to-valley contrast of the Pendellösung fringes degrades for the 700 °C piece, suggesting a poorer GaAs_{1-x}Bi_x/GaAs interface. This may explain the lower PL intensity in Figure 2(b). For the 800 °C piece, only a weak shoulder is observed with no well-defined GaAs_{1-x}Bi_x/GaAs interface. As expected, the PL peak energy measured at 10 K shows a blue-shift of 120 meV (PL spectra not shown), consistent with significant Bi out-diffusion as observed in the HR-XRD spectra.

FIG. 3. The HR-XRD curves of GaAsBi sample ($x = 0.065$) at different annealing temperatures.

FIG. 4. Temperature dependent (a) and room temperature (b) PL of as-grown and annealed GaAsBi with Bi content 0.04 and 0.048. Both samples were annealed at 700 °C for 30 s.

Localization effects in $\text{GaAs}_{1-x}\text{Bi}_x$ alloys using temperature dependent PL studies have been reported earlier.⁷ Here, we measured temperature dependent PL of as-grown and annealed $\text{GaAs}_{1-x}\text{Bi}_x$ pieces to assess the effects of annealing on localization and the results are shown in Figure 4(a). For the sample with $x = 0.048$, the annealed piece shows a less pronounced S-shape behavior compared to the as-grown piece. The 10 K PL peak energy blue-shifts by 6 meV and the PL FWHM reduces from 75 to 68 meV. For the $\text{GaAs}_{0.96}\text{Bi}_{0.04}$ pieces, the temperature dependent PL data are similar for the as-grown and the annealed pieces, with only 4 meV reduction in FWHM of the 10 K PL. For temperatures above 150 K, the PL peak energies of the as-grown and annealed pieces for both compositions ($x = 0.04$ and 0.048) are similar, showing that the band gap is not affected by annealing.

The growth conditions of the $\text{GaAs}_{0.96}\text{Bi}_{0.04}$ sample were altered compared to $\text{GaAs}_{0.952}\text{Bi}_{0.048}$ sample in order to reduce the localization effects and significantly weaker

localization was obtained, as shown in Figure 4(a). The $\text{GaAs}_{0.96}\text{Bi}_{0.04}$ sample was grown at 420 °C at a rate of 1 μm per hour while $\text{GaAs}_{0.952}\text{Bi}_{0.048}$ sample was grown at 400 °C at a rate of 0.16 μm per hour. The room temperature PL intensity of $\text{GaAs}_{0.96}\text{Bi}_{0.04}$ sample is ~6 times higher than the $\text{GaAs}_{0.952}\text{Bi}_{0.048}$ sample, as shown in Figure 4(b).

Since similar room temperature PL improvement ratio was achieved (~3 times) in samples with $x = 0.04$ and 0.048 through thermal annealing, whilst reductions in localization effects in both differs, we may conclude that the PL improvement obtained does not necessarily originated from the reduction of Bi inhomogeneity. The small reduction of the 10 K PL FWHM for both samples indicates that alloy fluctuations in $\text{GaAs}_{1-x}\text{Bi}_x$ are not easily removed by thermal annealing. Hence, the PL intensity improvement could be dominated by the reduction of other types of defects including arsenic and gallium related defects.

In summary, rapid thermal annealing has been carried out on MBE grown $\text{GaAs}_{1-x}\text{Bi}_x$ samples. Thermal annealing improves the optical quality of this low temperature growth alloy, without significantly affecting the PL peak wavelength. The PL intensity improvement may be dominated by the reduction of non-bismuth related defects as only a small improvement in Bi inhomogeneity was observed after annealing.

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