

## Photoluminescence and Raman Scattering of GaAs<sub>1-x</sub>Bi<sub>x</sub> Alloy (Kefotopendarcahayaan dan Serakan Raman pada Alooi GaAs<sub>1-x</sub>Bi<sub>x</sub>)

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### ABSTRACT

Photoluminescence (PL) and Raman spectra of GaAs<sub>1-x</sub>Bi<sub>x</sub> samples grown at different rates (0.09 to 0.5  $\mu\text{m/h}$ ) were investigated. The PL peak wavelength initially redshifted with the increase of growth rate and reached the longest wavelength (1158 nm) for sample grown at 0.23  $\mu\text{m/h}$ . This is followed by PL peak wavelength blueshift for higher growth rates. The Raman data show peaks at 162, 228, 270, and 295  $\text{cm}^{-1}$  which can be attributed to GaAs like phonons. GaBi like vibrational modes were also observed at 183 and 213  $\text{cm}^{-1}$ . However, the intensity of Bi induced phonons is significantly weaker compared to GaAs due to low concentration of Bi compared to As and thin GaAs<sub>1-x</sub>Bi<sub>x</sub> epilayer. The PL data and GaAs transverse optical (TO) to longitudinal optical (LO) phonons intensity ratio indicate that Bi concentration is highly dependent on the growth rate and the highest Bi concentration was obtained by sample grown at 0.23  $\mu\text{m/h}$ . It is found that the full-width-at-half-maximum (FWHM) of GaAs LO mode increases significantly for samples grown at high growth rates suggesting crystal quality degradation due to lack of surfactant effects.

Keywords: GaAsBi; photoluminescence; Raman spectroscopy

### ABSTRAK

Kefotopendarcahayaan (PL) dan spektrum Raman daripada sampel GaAs<sub>1-x</sub>Bi<sub>x</sub> yang ditumbuhkan pada kadar berbeza (0.09 hingga 0.5  $\mu\text{m/jam}$ ) telah dikaji. Pada mulanya, panjang gelombang puncak PL mengalami anjakan merah dengan peningkatan kadar pertumbuhan dan mencapai panjang gelombang tertinggi iaitu 1158 nm untuk sampel yang ditumbuh pada kadar 0.23  $\mu\text{m/jam}$ . Ini diikuti oleh anjakan biru pada kadar pertumbuhan yang lebih tinggi. Data Raman menunjukkan kehadiran beberapa puncak pada nombor gelombang 162, 228, 270 dan 295  $\text{cm}^{-1}$  yang disebabkan oleh fonon GaAs. Selain itu, mod getaran GaBi juga dapat diperhatikan pada 183 dan 213  $\text{cm}^{-1}$ . Namun, keamatan fonon GaBi jauh lebih lemah berbanding GaAs disebabkan kepekatan Bi yang rendah berbanding As dan lapisan GaAs<sub>1-x</sub>Bi<sub>x</sub> yang nipis. Data PL dan nisbah keamatan fonon optik melintang (TO) kepada fonon optik membujur (LO) GaAs menunjukkan bahawa kepekatan Bi sangat bergantung kepada kadar pertumbuhan dan kepekatan Bi yang tertinggi diperolehi oleh sampel yang ditumbuh pada kadar 0.23  $\mu\text{m/jam}$ . Kajian ini mendapati bahawa nilai FWHM untuk fonon LO GaAs meningkat dengan ketara untuk sampel yang ditumbuh dengan kadar pertumbuhan yang tinggi dan ini menunjukkan kemerosotan kualiti kristal disebabkan oleh pengurangan kesan surfaktan.

Kata kunci: GaAsBi; kefotopendarcahayaan; spektroskopi Raman

### INTRODUCTION

The development of new alloys based on GaAs is important to realize low cost optoelectronic devices operating in the optical fiber 2<sup>nd</sup> and 3<sup>rd</sup> operating windows and biomedical sensors operating in near infra-red region. The incorporation of Bi into GaAs to form GaAs<sub>1-x</sub>Bi<sub>x</sub> introduces many interesting properties such as relatively large band gap reduction and temperature insensitive band gap (Francoeur et al. 2003; Huang et al. 2005; Oe 2002; Tixier et al. 2003). The band gap reduction is obtained by the reduction of the conduction band minimum and the increase of valence band maximum with Bi incorporation.

The former can be estimated by using the Valence Band Anti-Crossing model while the later can be determined by using the virtual crystal approximation (VCA) (Alberi et al. 2007; Mohmad et al. 2014; Zhang et al. 2005). Based on these models, the required Bi concentration ( $x$ ) to obtain room temperature emission at 1.3 and 1.55  $\mu\text{m}$  is approximately 0.075 and 0.11, respectively.

Unfortunately, incorporating such high concentration of Bi into GaAs require a relatively low growth temperature (typically 270 to 400  $^{\circ}\text{C}$ ) and this lead to the formation of Ga and As related defects (Bertulis et al. 2006; Henini et al. 2007; Lu et al. 2008). Bi related defects may also present such as Bi antisites ( $\text{Bi}_{\text{Ga}}$  i.e Bi atom siting at Ga

site) (Kunzer et al. 1993). Increasing the Bi flux to obtain higher Bi concentration is limited by the formation of Bi droplets (Ptak et al. 2012). To date, incorporating high concentration of Bi into GaAs with minimum optical quality degradation remains a challenge. In order to obtain high quality GaAs<sub>1-x</sub>Bi<sub>x</sub>, an in-depth understanding on the effect of each growth parameters are important. The effect of growth temperature, Bi flux and Ga to As flux ratio have been reported by several groups (Bastiman et al. 2012; Lewis et al. 2012; Lu et al. 2008). In this work, we report the effects of growth rate on the quality and properties of GaAs<sub>1-x</sub>Bi<sub>x</sub> alloy. This work focuses on rapid and non-destructive techniques which are photoluminescence and Raman spectroscopy.

#### MATERIALS AND METHODS

GaAs<sub>1-x</sub>Bi<sub>x</sub> samples studied in this work were grown by molecular beam epitaxy (MBE) under ultra-high vacuum at the University of Sheffield. The MBE system consists of three elemental sources; Ga, As, and Bi and beam equivalent pressure for each source were calibrated prior

to the growth. The samples consist of undoped GaAs (100) substrate, 500 nm of GaAs buffer, followed by 25 nm GaAs<sub>1-x</sub>Bi<sub>x</sub> epilayer and capped with 50 nm of GaAs. For the GaAs<sub>1-x</sub>Bi<sub>x</sub> layer, growth temperature and temperature of the Bi cell were fixed at 370 and 520 °C, respectively. The growth rate was varied from 0.09 to 0.5 μm/h by increasing the Ga flux while maintaining the As to Ga beam equivalent pressure ratio at 23. The list of samples and growth parameters are summarized in Figure 1.

For photoluminescence (PL), measurements were carried out at room temperature using a continuous wave 532 nm laser, a monochromator (Horiba iHR320) and an electrically cooled InGaAs detector with cut-off wavelength of ~1650 nm. The laser beam was chopped at 180 Hz and a standard lock-in amplifier technique was used to reduce the signal to noise ratio. The vibrational spectra were measured using a confocal micro-Raman imaging spectroscopy (DXR2Xi, Thermo Scientific) with excitation wavelength of 532 nm (laser spot size of ~1 μm) and a CCD detector. The Raman instrument was calibrated based on the Si band peak position at 520.7 cm<sup>-1</sup>.

Material	Thickness (nm)	Sample	Growth rate (μm/h)
GaAs cap	50	i	0.09
GaAs <sub>1-x</sub> Bi <sub>x</sub> layer	25	ii	0.16
GaAs buffer	500	iii	0.23
S.I (100) GaAs substrate		iv	0.36
		v	0.5

FIGURE 1. (a) Structure and (b) growth rate of GaAs<sub>1-x</sub>Bi<sub>x</sub> samples studied in this work

#### RESULTS AND DISCUSSION

Figure 2(a) shows room temperature PL spectra of GaAs<sub>1-x</sub>Bi<sub>x</sub> samples ii to v grown at a rate between 0.16 and 0.5 μm/h. The PL spectrum for sample i (growth rate 0.09 μm/h) is too weak and is not shown. Based on the results, the PL peak wavelength for sample ii, iii, iv, and v is 1091, 1158, 1105, and 1080 nm, respectively. The PL peak wavelengths for all samples are significantly longer than the PL peak wavelength of GaAs (~870 nm) indicating successful incorporation of Bi into the GaAs lattice. The PL peak wavelength initially redshifted to 1158 nm with the increase of growth rate and then blueshifted to 1080 nm

for sample iv and v (Figure 2(b)). This observation suggests that Bi incorporation initially increases with the increase of growth rate but reduces for growth rate >0.23 μm/h.

Based on Mohmad et al. (2014), the estimated Bi concentration for sample ii, iii, iv, and v is 0.041, 0.052, 0.043, and 0.039, respectively. It is important to note that if Bi concentration is inhomogeneous across the GaAs<sub>1-x</sub>Bi<sub>x</sub> layer, room temperature PL measurements tend to estimate the maximum Bi content in the sample instead of the average Bi content (Mohmad et al. 2015). The incorporation of Bi into GaAs will cause the valence band maximum to increase due to the anti-crossing interaction

between the valence band of GaAs and the Bi resonant states (Alberi et al. 2007). The conduction band minimum also will decrease linearly with Bi concentration at a rate of 23 meV/%Bi leading to the reduction of the band gap (Mohmad et al. 2014).

PL full-width-at-half-maximum (FWHM) for samples ii-iv is between 73 and 88 meV. These values are relatively small compared to the literature (Bertulis et al. 2006; Lu et al. 2009; Tixier et al. 2003) and comparable

to the high quality GaAs<sub>1-x</sub>Bi<sub>x</sub> reported by Mohmad et al. (2011). Despite the relatively narrow PL FWHM, they are still much larger than the thermal distribution broadening at room temperature (~26 meV) which indicates significant alloy fluctuation and Bi clustering in the samples. However, the PL FWHM for sample v is significantly larger (138 meV) and the PL intensity is the lowest compared to other samples.

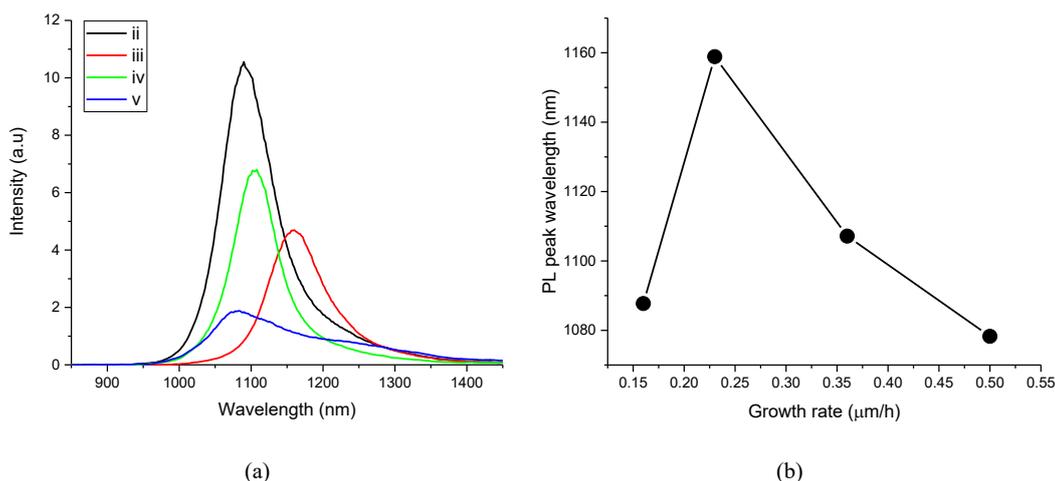


FIGURE 2. (a) PL of GaAs<sub>1-x</sub>Bi<sub>x</sub> samples measured at room temperature and (b) PL peak wavelength versus growth rate

In order to verify the effect of growth rate on the incorporation of Bi into GaAs, Raman spectroscopy measurements were carried out. Figure 3 shows Raman spectra of sample i to v. For each sample, Raman spectra were measured at three different positions and then averaged to obtain the final spectra. In order to see the vibrational modes clearly, an expanded view around the small wavenumber region was also plotted. Raman data show that the GaAs<sub>1-x</sub>Bi<sub>x</sub> samples show two-mode

behaviour which consists of GaAs and GaBi like vibrational modes. The two main peaks at 295 and 270 cm<sup>-1</sup> correspond to the GaAs LO and TO phonons while the peaks at 162 and 228 cm<sup>-1</sup> can be attributed to the GaAs 2TA and LA modes, respectively. Besides, two weak peaks at 183 and 213 cm<sup>-1</sup> were observed and consistent with the TO and LO vibrational modes of GaBi (Erol et al. 2017; Seong et al. 2005; Steele et al. 2014, 2013; Verma et al. 2001).

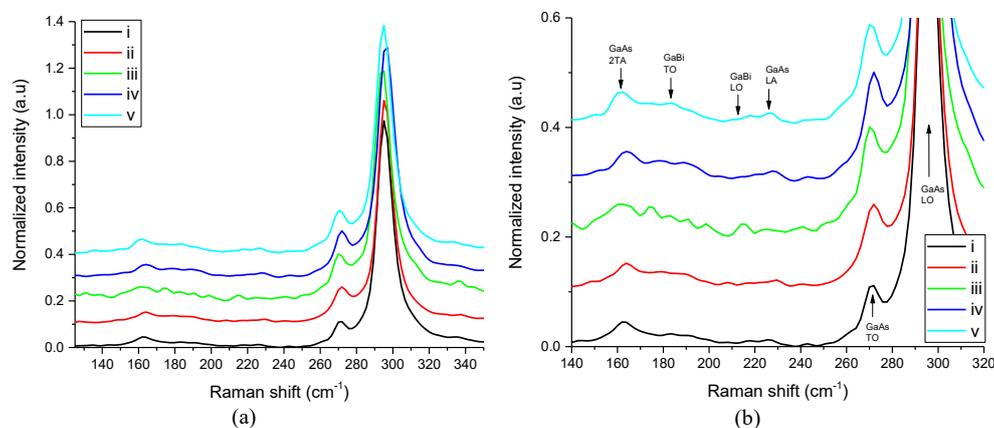


FIGURE 3. Raman spectra of GaAs<sub>1-x</sub>Bi<sub>x</sub> samples grown at different rates (a) full spectra and (b) expanded view around small wavenumber region. The spectra were normalized to the GaAs LO peak and vertically shifted for clarity

The observed two-mode behaviour is expected and consistent with other ternary III-V alloys. For example, Raman spectra of  $\text{GaAs}_{1-x}\text{P}_x$  show GaAs and GaP like phonon modes (Verma et al. 2001). Our results show that Bi related phonons are significantly weaker compared to GaAs phonons. This is mainly due to the low concentration of Bi compared to As and additionally in our case, due to thin  $\text{GaAs}_{1-x}\text{Bi}_x$  epilayer (25 nm). The intensity of the GaBi like phonons may be enhanced by increasing the laser power but this led to other undesirable effects such as GaAs peak broadening (results not shown). In comparison, most of the earlier works used uncapped bulk  $\text{GaAs}_{1-x}\text{Bi}_x$  with thickness between 0.2 and 1  $\mu\text{m}$  (Seong et al. 2005; Steele et al. 2014, 2013; Verma et al. 2001). Besides, it is important to note that due to the thin bismide layer, the measured Raman spectra originated from the  $\text{GaAs}_{1-x}\text{Bi}_x$  and the GaAs layer. The presence of GaBi TO and LO modes verify the incorporation of Bi into the GaAs

lattice. Seong et al. (2005) proposed that the  $213\text{ cm}^{-1}$  peaks originated from the substitutional Bi on As site while the  $183\text{ cm}^{-1}$  peak may be attributed to the Bi anti-site ( $\text{Bi}_{\text{Ga}}$ ). Unfortunately, it is difficult to establish a clear relationship between growth rate and GaBi like phonons based on our data due to the weak peaks.

Next, we analyze the two most prominent peaks which are the GaAs LO ( $295\text{ cm}^{-1}$ ) and TO modes ( $270\text{ cm}^{-1}$ ), as shown in Figure 4. The FWHM of GaAs LO phonon is  $\sim 10.3\text{ cm}^{-1}$  at low growth rates but increases to  $\sim 11.7\text{ cm}^{-1}$  for samples grown at  $>0.16\text{ }\mu\text{m/h}$ . The GaAs TO/LO intensity ratio initially increases from 0.12 to 0.21 with the increase of growth rate, reached a maximum at  $0.23\text{ }\mu\text{m/h}$  and decreases at higher growth rates. Based on Raman selection rules in a zincblende crystal, the GaAs TO mode is forbidden (Steele et al. 2013). It was proposed that the presence of GaAs TO mode is due to the relaxation of Raman selection rules as a result of Bi-induced disorder in the lattice (Steele et al. 2013).

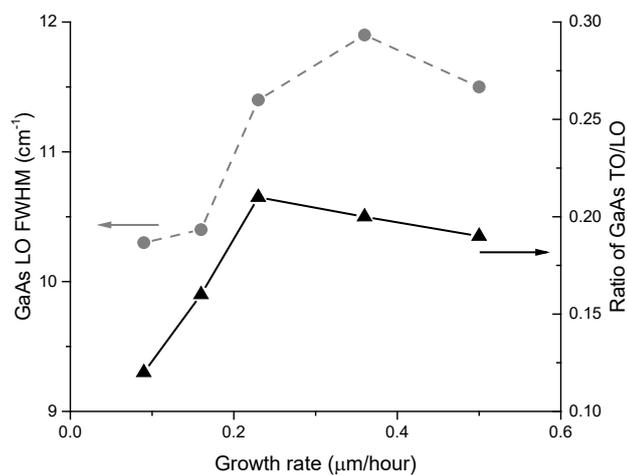


FIGURE 4. GaAs LO mode FWHM and intensity ratio between GaAs TO/LO versus growth rate

It is interesting to note that the trend of GaAs TO/LO ratio is similar to the trend of the PL peak wavelength shown in Figure 2. Sample iii ( $0.23\text{ }\mu\text{m/h}$ ) which has the highest GaAs TO/LO ratio also has the longest PL peak wavelength. This observation suggests that the GaAs TO/LO ratio may be used to indicate Bi incorporation as higher Bi will lead to more disorder and hence higher GaAs TO/LO ratio. It is well known that Bi adatoms tend to segregate to the surface during growth. By increasing the growth rate, higher fraction of Bi adatoms will be quickly buried into

the lattice and increases Bi incorporation. This explains PL peak wavelength redshift and the increase of GaAs TO/LO ratio for growth rates between  $0.09$  and  $0.23\text{ }\mu\text{m/h}$ . However, once the growth rate is too high, the significantly large Ga flux will dilute the Bi leading to reduced Bi incorporation and PL peak wavelength blueshift (Figure 2) (Ptak et al. 2012). Besides, the increase of GaAs LO FWHM with growth rate can be attributed to the reduction of surfactant effects as less Bi are segregated and accumulated on the surface at high growth rates. The

lack of surfactant will contribute towards higher density of defects and is consistent with PL intensity degradation shown in Figure 2.

#### CONCLUSION

PL peak wavelength of the GaAs<sub>1-x</sub>Bi<sub>x</sub> samples initially redshifted to 1158 nm with the increase of growth rate but blueshifted for growth rate >0.23 μm/h. Raman data show that the GaAs TO/LO intensity ratio follows a similar trend with the PL while the FWHM of GaAs TO mode increases with the increase of growth rate. These indicate that Bi incorporation initially increases with the increase of growth rate and reached a maximum at 0.23 μm/h. For samples grown at >0.23 μm/h, Bi incorporation reduces due to significantly high Ga flux compared to Bi leading to PL peak wavelength blueshift and reduction of the GaAs TO/LO ratio. The lack of surfactant effects is also evidenced with the increase of GaAs LO mode FWHM at high growth rates. Our finding suggests that Raman spectroscopy is a useful non-destructive tool to optimize the growth conditions of GaAs<sub>1-x</sub>Bi<sub>x</sub> alloy.

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