GaAsBi atomic surface order and interfacial roughness observed by STM and TEM

F Bastiman, Y Qiu and T Walther
Department of Electronic & Electrical Engineering, University of Sheffield, Sir Frederick Mappin Building, Mappin Street, Sheffield S1 3JD, UK

f.bastiman@sheffield.ac.uk

Abstract. GaAsBi is an interesting ternary material for opto-electronic applications. Bi fractions of 11-13% allow 1.55 µm emissions from a range of bulk and QW structures. GaAsBi has shown strong room temperature photoluminescence. The temperature insensitive band gap and large spin orbit splitting are attractive optoelectronic features, however the typical full width half maximum is 2.5 times greater than GaAs. In solid source molecular beam epitaxy (MBE), near stoichiometric fluxes and low growth temperatures are necessary to achieve the desired Bi content. In order to explore photoluminescence linewidth broadening and the accommodation of strain a joint scanning tunnelling microscopy (STM) and scanning transmission electron microscopy (STEM) study of quasi-bulk and QW structures has been undertaken.

1. Introduction
The bismuth alloy GaAs$_{1-x}$Bi$_x$ has a number of interesting properties, namely band gap reductions of 88 meV/% and large spin orbital splitting [1, 2]. The narrow, temperature insensitive band gap offered by such an alloy is particularly well suited to the fabrication of infra red emitters and photodetectors [2], however certain complications in the growth process have limited the impact of this alloy.

The strong tendency towards surface segregation and droplet formation of Bi during epitaxy has led to unconventional low temperatures growth parameters. Dilute bismuthides can be grown at around 430 °C up to ~1% Bi [3], however for high compositions lower growth temperatures are necessary. It is common to grow at temperatures as low as 280 °C in order to ensure high quality, smooth epitlayers are produced with >10% Bi fractions [4]. X-ray Diffraction (XRD) and photoluminescence (PL) data show high quality crystalline material with strong room temperature PL can be achieved. There are two restrictions to molecular beam epitaxy (MBE) growth of this ternary alloy. Firstly, in the 335 - 400 °C growth temperature range the film thickness/composition is restricted via strain related undulations and eventually dislocations. Secondly, below 335 °C undulations and dislocations are reduced due to thermal limitations, however point defects strongly affect material quality.

In this paper, scanning tunnelling microscopy (STM) and scanning transmission electron microscopy (STEM) are performed on samples grown at each of these limits in order to investigate observed XRD and PL phenomena.
2. Experiment

This work was performed on an Omicron MBE-STM system fitted with As₄, Ga, In, Bi and Mn effusion sources and RHEED for dynamic surface analysis. Full details of the system are discussed elsewhere [5]. An undoped on axis (± 0.1°) GaAs(001) epi-ready substrate was cleaved to 11 x 3.5 mm² in order to accommodate the sample mounting.

The samples were degassed with no further ex situ processing. The degas procedure entailed initial heating to a substrate temperature, \( T_s = 400 \, ^\circ C \) for 30 minutes, followed with heating to \( T_s = 600 \, ^\circ C \) under an As₄ flux for conventional oxide removal. The structure of sample LE2 featured an 80 nm buffer layer grown at 590 °C followed by cooling to 400 °C after which a 15 nm GaAsBi layer was deposited and capped with 30 nm of GaAs at the same temperature. To provide a sharper lower interface, the structure of sample B029 featured a thicker 160 nm buffer layer which was then annealed for 30 minutes at 600 °C to produce wide, flat terraces. After cooling to 320 °C, a 17 nm GaAsBi layer was deposited, followed by a 17 nm spacer, a further 4 nm QW and finally a 40 nm cap of GaAs. In each sample the RHEED showed a strong 2x1 reconstruction throughout the GaAsBi layer and an n\times3 reconstruction during the cap. With the exception of the buffer layer, all growth was performed at the initial GaAsBi growth temperature and the samples were not subject to high temperature anneals.

\( T_s \) values of 295 °C and 400 °C [6] were identified from As cap removal and \( c(4\times4)/(2\times4) \) transition in the absence of external flux, respectively. Samples were quenched for in vacuo scanning tunnelling microscopy (STM) imaging purposes before reheating and capped with GaAs for ex situ analysis. The (004) high resolution X-ray diffraction (HRXRD) \( \theta/2\theta \) scans of the as-grown samples were measured to verify crystal quality. 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 [7]. For the photoluminescence (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. Scanning transmission electron microscopy (STEM) was performed in a JEOL 2010F field-emission transmission electron microscope with scan unit and annular dark-field (ADF) and bright-field (BF) detectors, which was operated at 197 kV, with 0.25nm probe size, semi-angle of beam convergence of 9.5 mrad and an inner detection angle for ADF of ~50 mrad.

3. PL and XRD characterisation

The large lattice mismatch (~12%) between binary GaAs and theoretical GaBi (6.324 Å) [7] leads to compositional/thickness epitaxial limitations. Strong room temperature PL is observed from samples with 0-9% Bi, covering the PL spectrum from 872 to ~1400 nm. Whilst relatively thick bulk layers can be grown for <4% Bi, the strain causes undulations and eventually dislocations that limit the thickness of higher composition alloys. Furthermore, Bi segregation and Bi-Bi adatom interaction lead to the formation of Bi droplets for high Bi:As fluxes [8].

Undulations and surface roughness seem to have limited effects on GaAsBi PL intensity, however the full width at half maximum (FWHM) rapidly increases upon the formation of Bi droplets. Figure 1 shows the PL spectra for LE2 grown at 400 °C with a nominal 5.6 % Bi composition determined from the PL peak shift. The intensity is only half that of a similar prepared sample where care was taken to avoid droplet formation, however the FWHM has increased from 75 meV (not shown) to 109 meV. An XRD spectrum for the same sample is shown in figure 2. It is evident from the broad peaks and lack of interfacial fringes that the layer has poorly defined interfaces. Best fit simulation data further implies that the Bi composition is not homogeneous throughout the layer, which probably contains 6.0% and 2.2% domains.

Sample B029 was in turn grown to investigate the effect of low temperature growth on interface roughening and FWHM. The PL spectrum is shown in Figure 1, and displays two distinct peaks, one at 1555nm from the 17nm QW and one at 1458 nm from the 4nm QW. The thicker QW exhibits a
FWHM of 106 meV and the thinner QW of 94 meV. It is unclear whether the linewidth narrowing is due to quantum effects or is a function of compositional variation. The XRD spectrum for B029 exhibits strong interfacial fringes, indicating the presence of abrupt interfaces, however attempts to fit a single compositional simulation peak to the experimental data proved non-trivial. The difficulty arises from the different thickness of the QW, with the diffuse scattering from the thinner well and apparent compositional variation between the two GaAsBi layers. The 1555nm PL peak from the quasi-bulk 17nm layer indicates a Bi composition of ~11% from empirical fitting [9].

It is clear from Figure 1 that LE2 exhibits much strong RT-PL despite the interfacial roughness. The cause of the PL intensity reduction in B029 and the origin of the linewidth broadening will be discussed in the following sections.

**Figure 1.** Room temperature PL intensity spectra for LE2 (red) and B029 (black, with dotted fits for bulk and quantum well peaks)

**Figure 2.** Experimental and simulated XRD spectra for samples LE2 (lower profile) and B029 (upper profile)

4. **STM images**

Undulations are commonly observed in ternary alloys with significant lattice mismatch. Figure 3 shows the upper surface of the QW in LE2 immediately prior to capping. The undulations have an average period of ~400 nm and a peak-to-trough amplitude variation of 2 – 3 nm. Each undulation is formed from dense stacks of 2D islands that are anisotropic, displaying elongation in the [110] direction. The rough interfaces are certainly non-deal, especially for narrow QWs where thickness variation can affect the local band gap and quantum confinement. The undulation period protracts for both increasing thickness and Bi composition, however the amplitude of the undulations remains unchanged. The strain driven undulation clearly limits the thickness of smooth GaAsBi films at this composition, however the PL intensity of LE2 (Figure 1) is strong despite the rough interfaces.

Lowering the sample temperature enables both an increase of Bi incorporation and, for temperatures less than ~335 °C, the mechanism for undulation generation is thermally limited [4]. Figure 4 shows the upper surface of the 17 nm QW of sample B029. The larger pits are monolayer (ML) trenches and islands that are a feature of the buffer layer growth and anneal. The small, dense anisotropic islands are GaAsBi 2x1 islands. The limited thermal energy limits the adatom mobility leading to a larger number of smaller islands when compared to typical GaAs growth temperatures,
however the surfactant nature of Bi enables the growth of flat epilayers even at these reduced temperatures.

Before capping the lower temperature grown sample exhibits superior interfacial quality, as supported by the XRD spectra in Figure 2. However, despite this apparent improvement in the epilayer interface the PL spectrum is weaker than the higher temperature sample and the FWHM is of a comparable width.

**Figure 3.** 1500 x 1500 nm\(^2\) STM image of upper surface of the QW in LE2 prior to the capping layer

**Figure 4.** 1500 x 1500 nm\(^2\) STM image of upper surface of the 17nm QW in B029 prior to the capping layer

5. STEM observations

Annular dark field (ADF) scanning transmission electron microscopy (STEM) images of the buried layers in cross-section are shown for both samples in Figure 5a. The [001] growth direction is indicated by the arrow in each case. Imaging of the upper sample (LE2) revealed a number of discontinuities similar to the one shown in the centre of the image. These discontinuities are accompanied by a rough interface which is particularly pronounced in the stark contrast at the upper surface. Whilst the STM image of LE2 revealed the presence of this undulation, the presence of such discontinuities was not derivable from the images.

Figure 5b shows a higher magnification ADF image of a portion of LE2, highlighting the poor contrast at the non-abrupt interfaces. The tendency of Bi to surface segregate at the higher growth temperature appears to have affected the interface abruptness and presumably lead to a fractional depletion of the Bi content of the upper monolayers (ML).

In contrast, the lower sample in Figure 5a (B029) displays continuous layers across the entire width of the sample. The layer thickness also displays excellent uniformity and the interfaces are abrupt. It is clear that the growth is homogeneous across the sample and that the lower growth temperature hinders the surface segregation of Bi. The higher image contrast of sample B029 compared to LE2 indicates a higher Bi content of the GaAsBi layers. 

Figure 6a shows a higher resolution ADF-STEM image of B029 emphasising the strong contrast between the GaAs and GaAsBi layers. The profile data of Figure 6b reveals the upper interface of each QW is around 1nm wider than the lower interface. Indeed, the reduction of roughness from the GaAsBi-GaAs interface of the 17 nm QW to the GaAs-GaAsBi interface of the 4 nm QW reveals that the GaAs recovers toward a smoother state even at this lower growth temperature. This is probably due to the surfactant nature of the small amount of Bi that is always present during the spacer and cap
layer growth and causes the $n\times3$ reconstruction to be observed during growth. The tail in the profile of Figure 6b is probably due to Bi segregation.

The results of interfacial roughness from the two samples anti-correlates with observed PL intensity reduction, implying that the interface is not a dominant factor in establishing the PL intensity from GaAsBi QWs. Further, the FWHM is comparable in the PL data and so it is not clear that the interfacial roughness is contributing to the linewidth broadening. The different structure of the two samples prevents a direct comparison, but it can be assumed that the roughening and discontinuities in LE2 may contribute to the observed degradation in the PL linewidth, whilst the same type of degradation in B029 could be caused by anti-site and other low temperature growth defects. In order to explore the atomic structure of the buried layers, higher resolution STEM imaging of the atomic structure is clearly necessary.

![Figure 5](image1)

**Figure 5.** (a) ADF-STEM image of LE2 (top) and B029 (bottom). Arrows indicate growth direction. (b) ADF-STEM image at 250kX magnification of continuous section of LE2

![Figure 6](image2)

**Figure 6.** (a) ADF-STEM image of B029 (b) profile of rectangle in (a) exhibiting interfacial tail at the upper interface of the GaAsBi QW. The reduced contrast of the 4nm QW compared to the 17nm wide layer indicates a lower Bi content, e.g. around ~8% instead of ~11%.

The PL and XRD simulation provide two independent means of quantifying the Bi content of the structures. In all instances the data correlates to within 0.1%. Energy-dispersive X-ray spectrum (EDXS) analysis and quantification of Bi and Ga X-ray line intensities yields apparent Bi concentrations that vary with the lines used for quantification. EDXS data from the centre of the 17nm
QW of B029 is displayed in figure 7. Ga_L and Ga_K are clearly present around 1.1 and 10 kV, together with a number of smaller peaks that represent the Bi_M and Bi_L lines. Each line pair can provide a value for a composition estimate, along with a statistical fit error: 7.7±0.7% for Bi_M/Ga_K, 10.7±1.8% for Bi_L/Ga_L. No calibrated k-factors for any Bi X-ray lines are currently available (this is under investigation). All values are therefore based on the nominal k-factors of Oxford Instrument’s ISIS300 software. If we use pure GaAs as a reference, then the As_K/As_L ratio of 1.45±0.05 measured would imply a specimen thickness of \( t = 81±12 \text{nm} \) [10], which is realistic and can be fed into an absorption correction. A quantification of Bi_L or Bi_M lines relative to As_K and Ga_K then yields \( x_{\text{Bi}} = 9±1\% \), while the ratio quantification of Bi_L or Bi_M relative to As_L and Ga_L lines yields 13±4.1%. Again, the difference is systematically bigger than simple counting and fitting errors can explain. Coincidentally, the nominal composition of \( x_{\text{Bi}} = 11\% \) lies right between these two alternatives, indicating the need for k-factor calibration using a thickness series for GaAsBi of known composition.

Figure 7. Energy-dispersive X-ray spectrum (EDXS) from centre of 17nm thick layer of GaAsSb in above sample B029

6. Summary

PL linewidth broadening is not caused by interfacial roughness, especially in the case of the lower growth temperatures where abrupt interfaces are observed. Strong RT-PL is present in discontinuous, undulating layers. Sharp abrupt interfaces are possible at low temperature due to reduced segregation, however, the PL quality is significantly reduced, probably due to LT-growth which could lead to antisite and point defects. High resolution investigation will be necessary to identify the cause of linewidth broadening as MBE grown GaAsBi reaches strain and temperature driven compositional limits.

References
[1] Francoeur S, Seong MJ, Mascarenhas A, Tixier S, Adamecyk M and Tiedje T 2003 Appl. Phys. Lett. 82, 3874
[2] Fluegel B, Francoeur S, Mascarenhas A, Tixier S, Young EC and Tiedje T 2006 Phys. Rev. Lett. 97, 067205
[3] Bastiman F and David JPR 2011 J. Cryst. Growth, to be submitted
[4] Lu X, Beaton DA, Lewis RB, Tiedje T and Whitwick MB 2008 Appl. Phys. Lett. 92, 192110
[5] Bastiman F, Cullis AG, Hopkinson M and Green M 2008 Microscopy of Semiconducting Materials 2007, Springer Proc. in Physics 120, 471
[6] Reginski K, Muszalski J, Preobrazhenskii VV and Lubyshev DI 1995 Thin Solid Films 267, 54
[7] Janotti A, Wei S-H and Zhang SB 2002 Phys. Rev. B 65, 115203
[8] Bastiman F and David JPR 2011 J. Cryst. Growth, accepted
[9] Xianfeng L, Beaton DA, Lewis RB, Tiedje T and Yong Z 2009 Appl. Phys. Lett. 95, 041903
[10] Walther T 2010 Proc. 16th MSM conference, Oxford, J. Phys. Conf. Ser. 209, 012029