Growth and structural characterization of GaAsBi/GaAs multiple quantum wells

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Abstract
GaAsBi/GaAs multiple quantum well (MQW) p–i–n diodes are grown by molecular beam epitaxy. Transmission electron microscope images of the diodes show good agreement between the intended and measured MQW periods, but poor agreement between the intended and measured GaAsBi quantum well thicknesses. This is likely due to the incorporation of Bi from a physisorbed surface layer that takes a finite time to accumulate during growth. The diodes with more than 40 wells show dislocations that indicate strain relaxation. This is supported by x-ray diffraction analysis, which also suggests that the i-region of the 54 well diode is tilted with respect to the substrate.

Keywords: molecular beam epitaxy, GaAsBi, multiple quantum wells, transmission electron microscopy, x-ray diffraction

(Some figures may appear in colour only in the online journal)

1. Introduction
Multiple quantum well (MQW) solar cells were first proposed by Barnham and Duggan [1]. By introducing quantum wells (QWs) into the i-region of a p–i–n solar cell, the absorption edge of the cell can be extended without a corresponding reduction in the voltage of the cell. Initial work on MQW solar cells was hindered by strain relaxation within the MQW region, which causes a significant increase in the dark current of the cell; reducing its efficiency [2]. The implementation of strain balancing in MQW solar cells allowed for thick MQW regions to be grown without exhibiting lattice relaxation [3]; this innovation yielded an order of magnitude decrease in the dark current of the cells.

Multi-junction solar cells require precise tuning of the band gaps of the component junctions in order to achieve optimal efficiency. There is a drive to produce a 1 eV material lattice matched to Ge to push the efficiency of multi-junction solar cells to 50% [4]. Batches of commercial multi-junction solar cells containing MQW top and middle junctions have shown median efficiencies in excess of 41% [5]. The difficulties in strain balancing highly mismatched MQW regions have limited the absorption edge of the incumbent middle junction material system, InGaAs/GaAsP, to <1000 nm (~1.2 eV) [6]. The incorporation of In into GaAs yields a band gap reduction of ~250 meV% strain, whereas the incorporation of Bi yields a band gap reduction of ~750 meV% strain. Replacing the InGaAs QWs with GaAsBi QWs will allow for easier tuning of the subcell absorption edges and contribute to the development of 50% efficient solar cells.

In order to undertake effective strain balancing of the GaAsBi system, it is important to first understand the strained GaAsBi/GaAs system. This paper investigates the growth and characterization of GaAsBi/GaAs MQW p–i–n diodes.

2. Experimental
The diodes characterized during this work were grown using an Omicron molecular beam epitaxy–scanning tunnelling
microscopy (MBE–STM) system. The diodes were grown on 11.4 × 11.8 mm substrates cleaved from 2″, epiready, n+ (Si doped), on axis ±0.1° GaAs substrates. The system calibration and sample preparation methods are discussed elsewhere [7]. The designs of the diodes grown during this work are shown in figure 1.

The growth rate used for the GaAs and GaAsBi regions was 0.55 μm h⁻¹ and that used for the AlGaAs regions was 0.79 μm h⁻¹. The Bi flux used for each sample was 0.24 atoms nm⁻² s⁻¹. The GaAs and AlGaAs regions were grown at 580 °C using As₂ and the GaAsBi region was grown at 380 °C using As₄. The As species was changed for the GaAsBi growth because it has been shown that there is a larger range of atomic As fluxes that gives rise to good quality GaAsBi when using As₄ compared to As₂ [7]. Growth of the first QW was preceded by the deposition of a Bi prelayer by the exposure of the surface to a Bi flux for 30 s. During this time the surface reconstruction changed from c(4 × 4) to c(n × 8), indicative of the presence of Bi in the surface reconstruction. This was done to avoid the compositional variation in the first few nm of GaAsBi growth due to the accumulation of a surface Bi layer as reported by Fan et al [8]. Growth was paused for 1 min at each barrier/well interface to prevent the build-up of excess Bi on the growth surface. It has been shown that the lifetime of a static Bi surface reconstruction at these temperatures is significantly longer than 30 s [7], so this pause was assumed to have no effect on the Bi chemisorbed on the sample surface. The extended growth at high temperature after the deposition of the MQW region will have annealed the GaAsBi QWs. It has been shown that annealing up to 600 °C for 15 min has negligible effect on the structural properties of GaAsBi [9, 10], so it was assumed that the effects of Bi diffusion during the unintentional annealing step could be ignored.

Transmission electron microscopy (TEM) specimens were prepared parallel to [110] using standard methods and examined in a JEOL 2000FX TEM operating at 200 kV. Magnification was calibrated to <0.5% using a superlattice structure with period measured by x-ray diffraction to an accuracy better than 0.1%. Reciprocal space maps (RSMs) about the GaAs 004 reflection were performed on a Panalytical X’Pert Pro MRD diffractometer equipped with a hybrid monochromator, giving pure Cu kα₁ (1.540598Å) radiation and a diffracted beam 3-bounce analyzer crystal.

### 3. Results and discussion

Typical TEM images from QW40 and QW54 are shown in figure 2. No dislocations are visible in QW40 (figure 2(a)), whereas they are clearly visible in QW54 (figure 2(b)). No dislocations were observed in QW05, QW20 or QW40; however, 60° dislocations at the MQW/AlGaAs interfaces were visible in QW54 and QW63, as expected for misfit dislocations that produce strain relaxation [11]. Some dislocations were also found in the AlGaAs cladding, below the GaAsBi layer, in QW54 and QW63. These dislocations were usually found close to clusters of misfit dislocations, such as the two dislocations in figure 2(d) in the AlGaAs layer below three interfacial misfit dislocations. It is probable that these are misfit dislocations expelled from the interface by repulsive interactions. For clarity, figures 2(c) and (d) show the AlGaAs/GaAsBi interfaces in QW40 and QW54 at higher magnification.

Upon initial inspection of the TEM images, the thicknesses of the QWs in each sample appeared to be quite uniform, as shown for QW40 in figure 3. In order to verify the QW thicknesses in each sample, the TEM images were analyzed as follows. The thicknesses of the component layers of the MQW were measured using the intensity of the dark field 002 image as a function of distance in the growth direction (e.g. QW20, figure 4). Interface positions (green) were assumed to lie at the point of maximum of the numerical gradient (magenta).

The average QW thicknesses and total MQW thicknesses calculated using this method are shown in table 1. This
analysis was not performed for QW63 as the barriers were too thin to provide reasonable data. The standard deviation of the QW widths throughout most of the MQWs was \( \sim 0.2 \) nm; QW05, however, showed a standard deviation of \( \sim 0.6 \) nm, which may be due to the small number of wells. In each MQW, the well grown first was thicker than the subsequent wells. This is in contrast to the results of Ludewig et al [12], who observed that the first well grown by MOVPE is thinner than the subsequent wells. The difference can be explained by the application of a Bi prelayer in this work. The Bi prelayer may cause there to be a larger physisorbed surface Bi layer for the first well than is present for subsequent wells. The growth by Ludewig et al did not involve such a prelayer, necessitating the build-up of a surface Bi layer to achieve Bi incorporation during the growth of the first well, and reducing the apparent width of the well.
The MQW region periods are all within 10% of their intended values; however the QW thicknesses are all <70% of their nominal values. The good agreement between the predicted and measured MQW periods suggests that the growth rate was accurately calibrated and the discrepancy between the predicted and measured QW thicknesses can be attributed to the Bi incorporation mechanism. It has been suggested that Bi incorporates into GaAs from a surface Bi layer formed during growth [13] and it has also been shown that a Bi terminated reconstruction can persist on a growing GaAs surface in the absence of a Bi flux [14]. It seems, therefore, that, while Bi incorporates from a chemisorbed surface reconstruction Bi layer, the presence of a physisorbed Bi layer on top of the reconstruction layer is required to allow the Bi in the surface reconstruction layer to incorporate. In this work, the physisorbed Bi layer probably desorbs or incorporates through the reconstruction layer during GaAs barrier growth and it is necessary to accumulate a new physisorbed surface Bi layer during the growth of each QW. This process will cause the Bi content in the QWs to vary as a function of position as seen in figure 4. If the time taken to accumulate a Bi surface after the Bi shutter is opened is greater than the time taken for it to either desorb from the substrate or incorporate into the spacer layer once the Bi shutter is closed, then the wells will appear thinner than intended. The two surface layers and the effect of Bi surface layer build-up and depletion are shown in figure 5.

The use of a valved Bi source would allow the Bi flux to be varied throughout QW growth, meaning that a high Bi flux could be used to rapidly accumulate a physisorbed Bi layer and then a low Bi flux could be used to produce a uniform Bi content in the wells. It is also possible that the Bi in the wells diffused out during the unintentional annealing from the growth of the cladding layers after the MQW region growth. This effect was assumed to be small based on previous investigations [9, 10].

To investigate the onset of dislocations in QW54, RSMs were taken of QW40 and QW54 at several angles around the surface normal (φs) of each diode. These scans are shown in figure 6. The MQW region of QW54 appears to be tilted with respect to the substrate as evidenced by the offsetting of the superlattice peaks in ω with respect to the substrate peak [15]. The broadening of all of the peaks in QW54 compared to those of QW40 is also indicative of strain relaxation within the MQW region [15]. The magnitude of the MQW region tilt in QW54 was calculated to be 0.045 ± 0.005°.

Analysis of the photoluminescence spectra (not shown) using the valence band anticrossing model [16] and approximating the confinement in the GaAsBi wells using the method of Singh [17] suggests that the average Bi content of the wells across all the samples is around 4.4%. The onset of dislocation generation appears to occur between 40 and 54 wells in the 620 nm MQWs in this work. The average strain calculated using the method of Griffin et al [2] for each of these samples is 0.17% (QW40) and 0.24% (QW54). Griffin et al estimated that that the onset of dislocation generation would occur at an average strain of ~0.24% for a 620 nm InGaAs/GaAs MQW. The result from this work suggests that GaAsBi/GaAs and InGaAs/GaAs MQWs may have comparable tolerances to strain.

4. Conclusions
GaAsBi/GaAs MQW p–i–n diodes were grown by MBE. TEM images of the MQW regions showed good agreement between the designed and measured MQW region periods, whereas there were significant differences between the designed and measured QW thicknesses. This suggests that the accuracy of the widths of the QWs is limited by the need to accumulate a physisorbed surface layer of Bi for Bi incorporation and the rapid desorption/incorporation of this Bi layer in the absence of a Bi flux. XRD RSM analysis of QW40 and QW54 showed evidence of strain relaxation and a tilting of the MQW region in QW54.

Figure 5. Diagram of the physisorbed and chemisorbed Bi layers and the predicted shape of the QWs based on the accumulation and depletion of the Bi surface layer.
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Table 1. QW and MQW layer thicknesses calculated from TEM. The nominal MQW thickness was 620 nm and the nominal QW thickness was 8 nm.

| Diode | MQW period (nm) | Difference from nominal MQW period (nm) | Difference from nominal MQW period (%) | QW thickness (nm) | Difference from nominal QW thickness (nm) | Difference from nominal QW thickness (%) |
|-------|-----------------|----------------------------------------|----------------------------------------|------------------|------------------------------------------|------------------------------------------|
| QW05  | 97.6 ± 0.6      | 7.4                                    | 7.0                                    | 44.4 ± 0.2       | 3.6                                      | 45.1                                      |
| QW20  | 27.8 ± 0.6      | 2.2                                    | 7.3                                    | 48.0 ± 0.3       | 3.2                                      | 39.9                                      |
| QW40  | 14.2 ± 0.6      | 1.1                                    | 6.9                                    | 49.0 ± 0.3       | 3.1                                      | 39.3                                      |
| QW54  | 11.2 ± 0.6      | 0.2                                    | 2.2                                    | 56.0 ± 0.3       | 2.4                                      | 29.9                                      |

Figure 6. $2\theta-\omega$ versus $\omega$ reciprocal space maps about the GaAs 004 reflection for (a) QW40 and (b) QW54. Horizontal lines have been added to the RSMs to highlight the offsetting of the SL peaks from the substrate peak. Note that the AlGaAs cladding layer peak is clearly visible for QW40 but has merged with the substrate peak for QW54. (c) The geometry of the sample on the diffractometer. (d) The tilting of the QW54 MQW region with respect to the substrate was measured by fitting the observed offsets of the SL peaks from the substrate peak as a function of $\phi_s$ with a sine curve. $\Delta \omega$ was measured for each SL peak at each value of $\phi_s$; the offset of each peak is individually plotted at each angle and the line of best fit takes all of the data points from QW54 into account.

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