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Influence of Growth Conditions on the Structural and Opto-electronic Quality of GaAsBi

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Abstract

A systematic series of GaAsBi pin diodes was grown by MBE using different growth temperatures and Bi fluxes, to study the effect on the structural and opto-electronic properties of GaAsBi. The Bi contents of the diodes show both growth temperature and Bi flux dependences. The diodes grown at higher temperatures show evidence of long range inhomogeneity from X-ray diffraction (XRD) measurements, whereas samples of comparable Bi content grown at lower temperatures appear to have well defined, uniform GaAsBi regions. However, the high temperature grown diodes exhibit more intense photoluminescence (PL) and lower dark currents. The results suggest that growth temperature related defects have a greater influence on the dark current than bismuth related defects, and therefore GaAsBi devices should be grown at the highest temperature possible for the desired Bi content.

Key Words

A1. High resolution X-ray diffraction
A3. Molecular beam epitaxy
B1. Bismuth compounds
B2. Semiconducting ternary compounds
B3. Heterojunction semiconductor devices
B3. Infrared devices

Highlights

- GaAsBi pin diodes with similar bismuth contents grown using different conditions
- Degradation of epilayer homogeneity at high growth temperatures
- Low growth temperature related defects have a large effect on dark current
- Bismuth related defects have a smaller effect on dark current of diodes

Introduction

The incorporation of bismuth into GaAs induces a large decrease in the band gap energy per unit strain [1], and a large increase in the spin-orbit splitting [2]. This band engineering capability makes GaAsBi a promising material for a wide range of opto-electronic applications such as photovoltaics [3] [4], detectors [5], lasers [6], and spintronics [7].

However, the growth of GaAsBi has proven challenging, with the Bi incorporation dependent on the growth temperature and the source fluxes of all three constituent species [8]. Additionally, the Bi atoms tend to segregate and form into droplets on the growing surface. Since the first demonstration of MBE-grown GaAsBi [9], significant progress has been made in the growth of epilayers with high Bi fractions [8] [10] and electrical devices fabricated therefrom [6] [5].

More recently, researchers have examined the evolution of optical properties and material defects under different growth conditions. The optimal growth rate for droplet-free surfaces and highest crystal quality was found to be dependent on the desired Bi content [11] [12]. The growth temperature was found, via temperature dependent PL, to affect the density of shallow and deep electronic states in the band gap [13]. An order of magnitude decrease in the hole trap concentration in GaAsBi was identified when the growth temperature was increased from 330 to 370 °C [14]. The use of UV illumination and a partial Bi wetting layer during growth has also been investigated, and resulted in PL emission with a significantly narrower linewidth than previously reported [15].

However, there have not been any studies into the diode properties of GaAsBi at a constant Bi content depending on the growth conditions. The aim of this paper is to provide some insight into the growth conditions that produce the best opto-electronic device performance for a given Bi incorporation. In this investigation, the dark current and photoresponsivity of a set of GaAsBi pin diodes was analysed. Two of the diodes contain a similar Bi content (1.3%), despite being grown using different substrate temperatures and Bi fluxes. Similarly, another two of the diodes contain 2.2% Bi. These two sets of diodes offer the opportunity to independently examine the influence of the growth temperature and the Bi content on the structural and opto-electronic properties of GaAsBi.

Experimental

Sample Growth

All epilayers were grown on GaAs (001) n+ substrates, using solid source MBE, in a pin diode structure - see figure 1. After outgassing, the surface oxide was removed at 600 °C. Growth temperatures quoted in this work were calibrated using RHEED transitions and have a precision of ± 3 °C, however the uncertainty is approximately ± 10 °C. The only difference between the epilayers is the growth parameters used for the GaAsBi layer. A 300 nm n-type GaAs buffer was grown using As_2 [16] with a dopant concentration of 2×10^{18} cm^{-3}. The GaAs deposition rate was measured using RHEED oscillations after the growth of the buffer layer, and the gallium cell temperature was adjusted to give a growth rate of 0.600 ± 0.010 ML/s. The GaAs growth took place at 577 °C using an As:Ga atomic flux ratio of approximately 1.6:1. The substrate and As cracker were cooled down for the GaAsBi growth over an approximately 20 minute period.

GaAs:Be p++	577 °C	<10 nm
GaAs:Be p+	577 °C	300 nm
GaAs	T_{grow}	10 nm
GaAsBi	T_{grow}	100 nm
GaAs:Si n+	577 °C	300 nm
GaAs:Si n+	Substrate	350 µm

Figure 1: GaAsBi pin diode structure, showing growth temperatures and layer thicknesses

T_{grow} (°C)	Bi BEP ($x10^{-8}$ mBar)	Bi content from PL (%)	Bi content from XRD (%)
355	10.6	3.6	3.51
375	10.6	3.2	3.25
385	10.6	2.7	2.82
395	10.6	2.2	2.19
405	10.6	1.3	1.37
375	5.0	1.2	1.31
375	7.6	2.2	2.25
375	10.6	3.2	3.25
375	15.0	4.0	4.12
375	21.2	5.3	5.37

Table 1: devices studied in this work, including growth parameters and key results from XRD and PL measurements, one of the epilayers (3.25% Bi) is shown twice in the table as it is part of both series

Prior to the growth of the GaAsBi layer, the Bi shutter was opened. After a short time (20-40 seconds depending on growth conditions) the RHEED pattern underwent a transition from an arsenic terminated c(4 x 4) to a Bi terminated (n x 3) reconstruction [17]. At this point the growth of the GaAsBi was started immediately, and the RHEED pattern changed to (n x 1). This was done to ensure that a thin wetting layer of Bi built up on the surface [8]. If the wetting layer is too thick then it is possible that this could result in an increased Bi content near the start of the epilayer, as seen in [18]. The GaAsBi i-region was grown using As_4[10] [19], and was designed to be 100 nm thick. Using a thicker i-region would provide greater insight into the diode light absorption; however, there is no guarantee that the GaAsBi layers would be pseudomorphic for the samples with higher Bi content, which would obfuscate any comparative characterisation.

The As:Ga flux ratio was close to 1:1 for all the epilayers. The growth parameters (substrate temperature and Bi beam equivalent pressure (BEP)) for the GaAsBi layers were varied systematically throughout the series - see table 1. A 2-minute pause followed the growth of the GaAsBi layer before a 10 nm GaAs spacer was grown using As_4. This was done to provide a relatively abrupt interface by covering the GaAsBi layer prior to raising the temperature, to prevent diffusion of the Bi atoms to the surface. The p-type GaAs layer was grown using As_2 with a dopant concentration of $4x10^{18}$ cm^{-3}. The surface was held at 577 °C for approximately 45 minutes for the growth of the upper GaAs layers; the GaAsBi was annealed during this step.

From table 1, there are two pairs of samples which contain a similar Bi content (1.31, 1.37, 2.19, and 2.25% Bi), despite being grown under different conditions. The uncertainty in the Bi content as measured by XRD and PL is ± 0.05% and ±0.2% respectively.

X-Ray Diffraction

A Bruker D8 Discover X-ray diffractometer was used to measure ω-2θ (004) XRD scans - see figure 2. The scans were simulated using Bede Rads Mercury software.

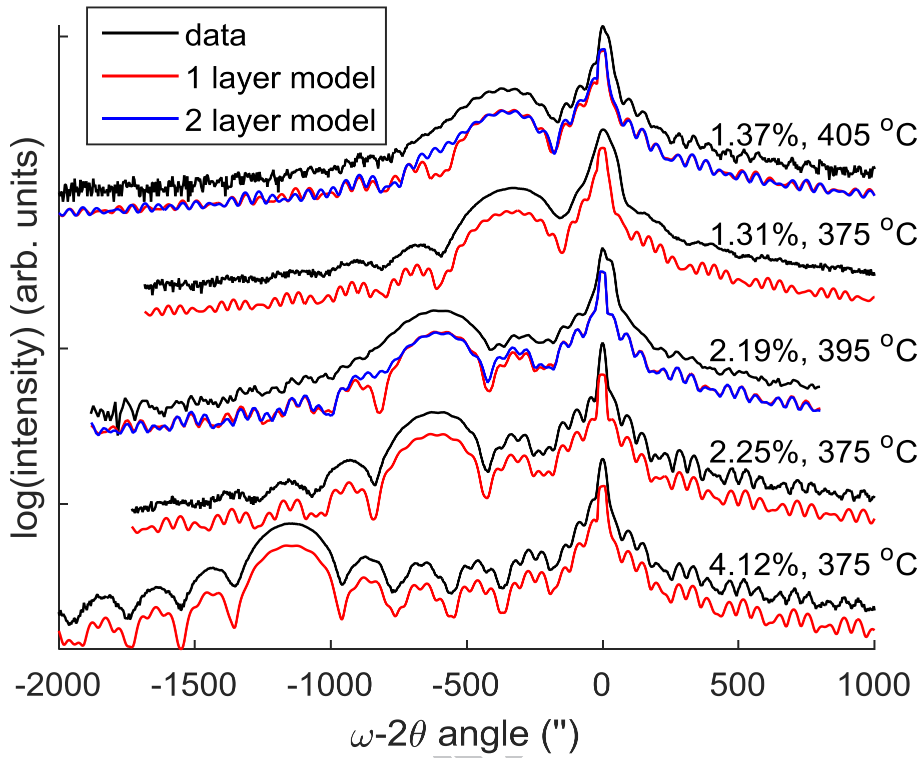


Figure 2: XRD scans and simulations of several of the epilayers relative to the GaAs diffraction peak, offset for clarity. The annotations denote the Bi content and growth temperature

The GaAsBi layers are all fully strained and are between 85 and 96 nm thick, which is thinner than the intended thickness of 100 nm. This is probably caused by shutter transients in the Ga cell.

From figure 2, thickness fringes caused by the GaAsBi layers are visible for the 1.31, 2.25, and 4.12% Bi epilayers. There are also fringes with a smaller period visible for the epilayers apart from the 1.31% Bi epilayer, which are caused by the thicker p-type GaAs layers. The presence of these thickness fringes is a qualitative indication of interface smoothness and layer homogeneity. However, for the epilayers grown at higher temperatures (1.37 and 2.19% Bi) the GaAsBi fringes are difficult to identify, and the GaAsBi diffraction peak is significantly broadened. These samples were initially modelled as containing a single uniform GaAsBi layer, but the simulation was altered to model the GaAsBi region as comprising two layers with different Bi contents, with the results plotted in figure 2. This approach produced a better fit to the data, and implies that the Bi incorporation is non-uniform in the growth direction for the higher temperature grown layers. The two layer XRD simulations returned structures with a marginally higher Bi content near the substrate. For example, the epilayer containing 2.19% Bi is better fit using a model comprising 54 nm (2.38% Bi) followed by 40 nm (1.89% Bi). This Bi incorporation profile is similar to the effect seen in [18], and arose during growth as all the epilayers were subject to the same in-situ annealing. Further measurements are planned to measure the Bi incorporation profile in the layers in more detail.

The XRD results suggest that growth at temperatures below 395 °C improves the interface quality and material homogeneity.

Photoluminescence Spectroscopy (PL)

The epilayers were irradiated at room temperature with a 532 nm CW laser with an excitation density of 120 W/cm^2. The emitted PL was directed into a monochromator. An LN_2 cooled Ge detector was used to measure the spectra, with a phase sensitive detection method. The measured spectra are plotted in figure 3. The Bi content in each epilayer calculated from the PL peak wavelength [20] is in excellent agreement with the value calculated using XRD (see table 1 for a comparison).

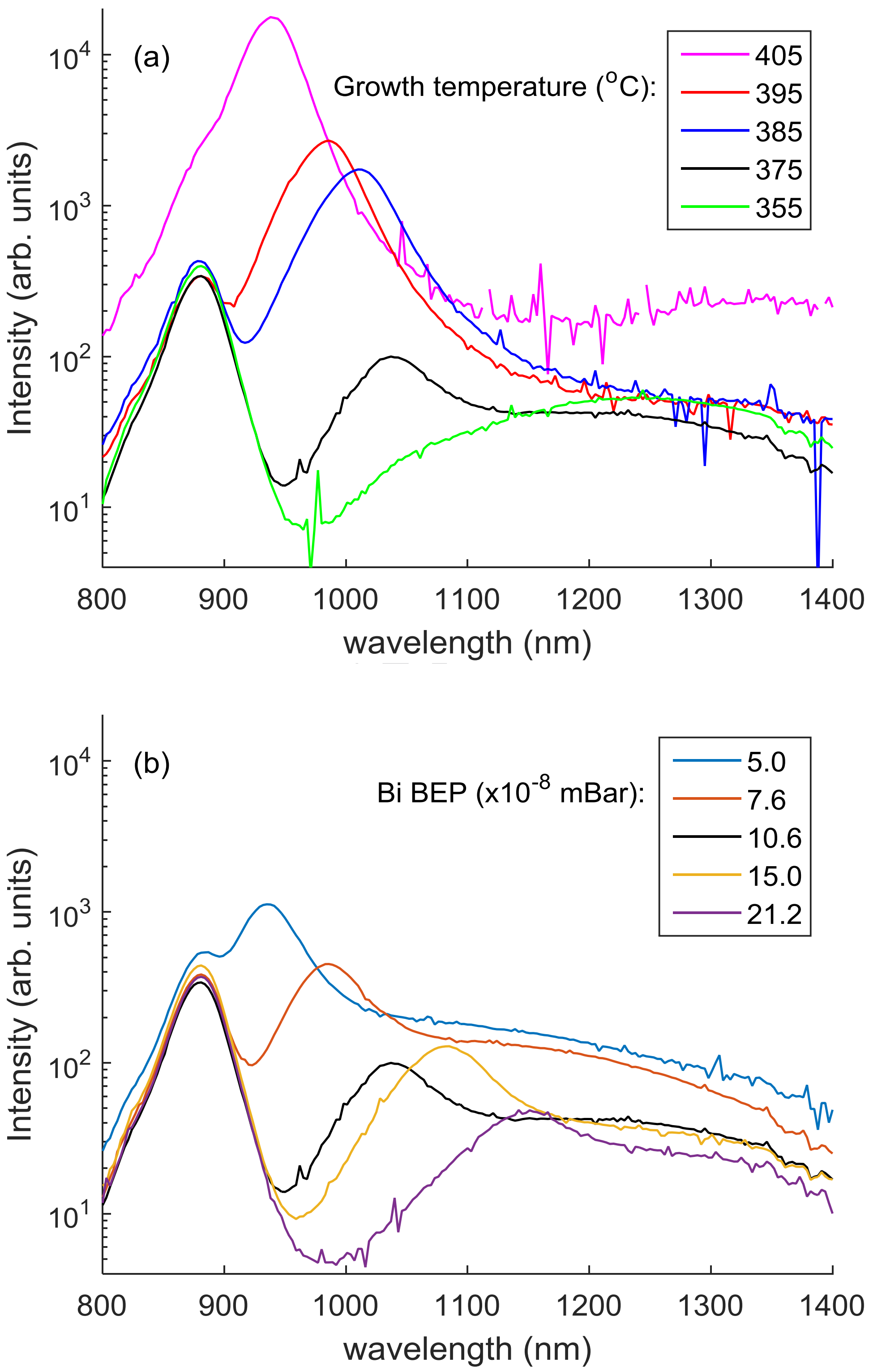


Figure 3: PL spectra of GaAsBi epilayers. (a) Epilayers grown at different temperatures with the same Bi BEP (10.6×10^{-8} mBar). (b) Epilayers grown with different Bi BEPs at 375 °C. Both graphs are on the same y-axis scale

From figure 3(a) an increase in the Bi BEP (at a constant growth temperature) results in longer wavelength PL emission and a lower emission intensity. Decreasing the growth temperature (at a constant Bi BEP) has a similar effect (from figure 3(b)). The PL signal around 1060 nm from the coldest grown epilayer (grown at 355 °C) is barely visible as a shoulder on the substrate PL. The weak, broad luminescence around 1200 nm is due to dopants in the GaAs layers and substrate, as this signal is still detected when measuring unused GaAs n-type substrates.

The decrease in PL peak intensity with increasing Bi content is similar to the results in [13] and [21]. However other studies have found that the PL peak intensity increased with increasing Bi content up to 4.5% Bi [22], attributed to improved carrier confinement [23]. The authors of [22] and [23] controlled the Bi content by optimising the As flux, Bi flux, and growth temperature. In this case, presumably they aimed for the highest PL intensity they could achieve at a given Bi content, meaning that a comparison with this work is not valid.

The PL peak intensity of the epilayers is plotted in figure 4 as a function of Bi content.

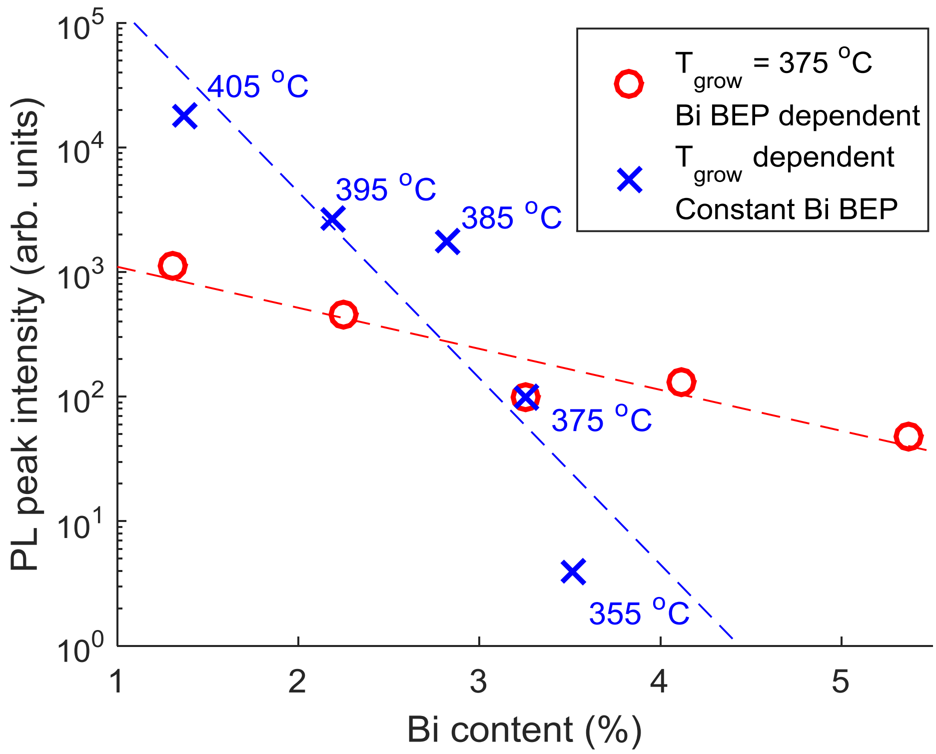


Figure 4: PL peak intensity as a function of Bi content for the two series of GaAsBi epilayers. The annotations denote the growth temperature of the layers.

From figure 4, the PL peak intensity decreases exponentially as the Bi content increases for both series of epilayers. The change in intensity is greater for the series grown at different temperatures. Comparing the two epilayers containing ~1.3% Bi (and the two containing ~2.2%), the epilayers grown at higher temperatures show more intense PL emission. This, and the trend shown by the other epilayers, implies that defects related to the growth temperature have a greater effect on the luminescence intensity of GaAsBi than bismuth related defects. The identity of these defects is unclear. In [24] it was found that rapid thermal annealing at 600 °C completely quenches As_{Ga} anti-site defects in GaAsBi. The same authors noted that no Bi_{Ga} anti-site defects were present in their epilayers. Further work is required to identify the defects present in these epilayers.

Bismuth has been observed acting as a surfactant in As rich growth of GaAsBi, and as an anti-surfactant during Ga rich growth or near stoichiometric growth [25]. The layers in this work were all grown using a 1:1 As:Ga flux ratio, so one would expect the formation of Ga droplets on the surfaces. Droplets on the surface will scatter the laser light and result in a reduced PL intensity. The samples do indeed show a low surface coverage of droplets, but it is not clear if these comprise Ga, Bi, or background impurities incorporated from the growth chamber.

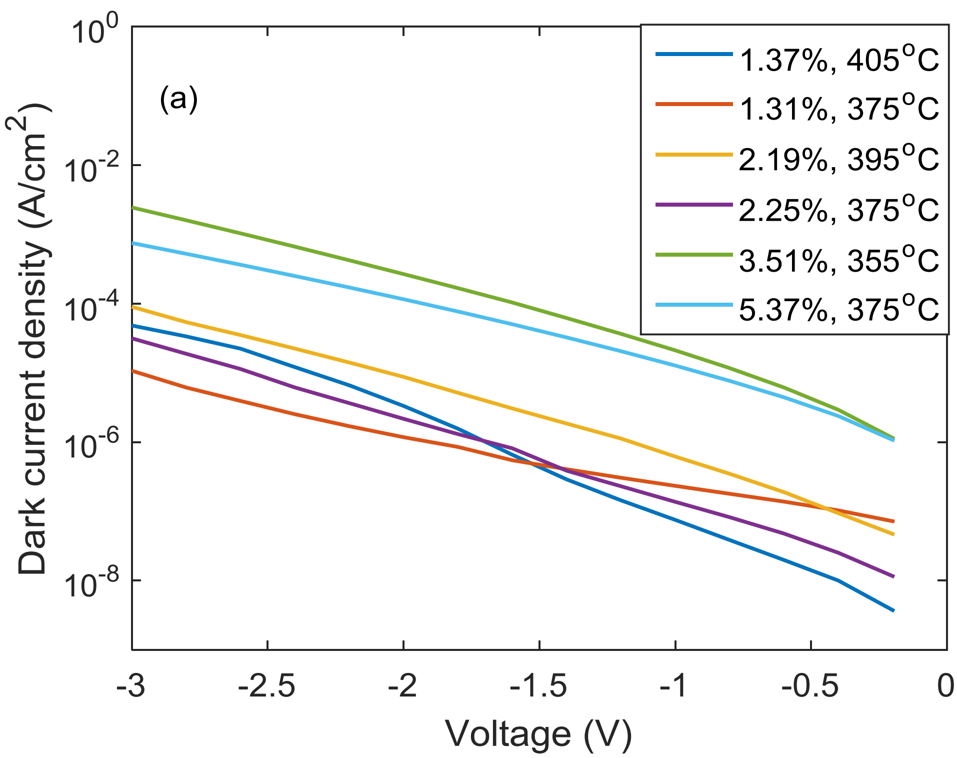
The room temperature PL measurements show that growth at higher temperatures produces epilayers with higher PL intensity, for the same Bi content.

The luminescence as a function of temperature was also measured between 12 and 300 K (not shown here) using a cryostat. The results are similar to those in [13], namely the emergence of sub-bandgap emission which is more prominent for the layers grown at lower temperature, as the cryostat temperature decreases. The authors of [13] concluded that localised Bi cluster states were responsible for the sub-bandgap emission.

Current-Voltage

The epilayers were fabricated into mesa devices with annular contacts on the front, and a common back contact. Current voltage measurements were taken in the dark and converted to current density data - see figure 5. The compliance limit was set to 100 mA.

The reverse and forward dark current densities of several of the diodes are plotted in figures 5(a) and 5(b) respectively.



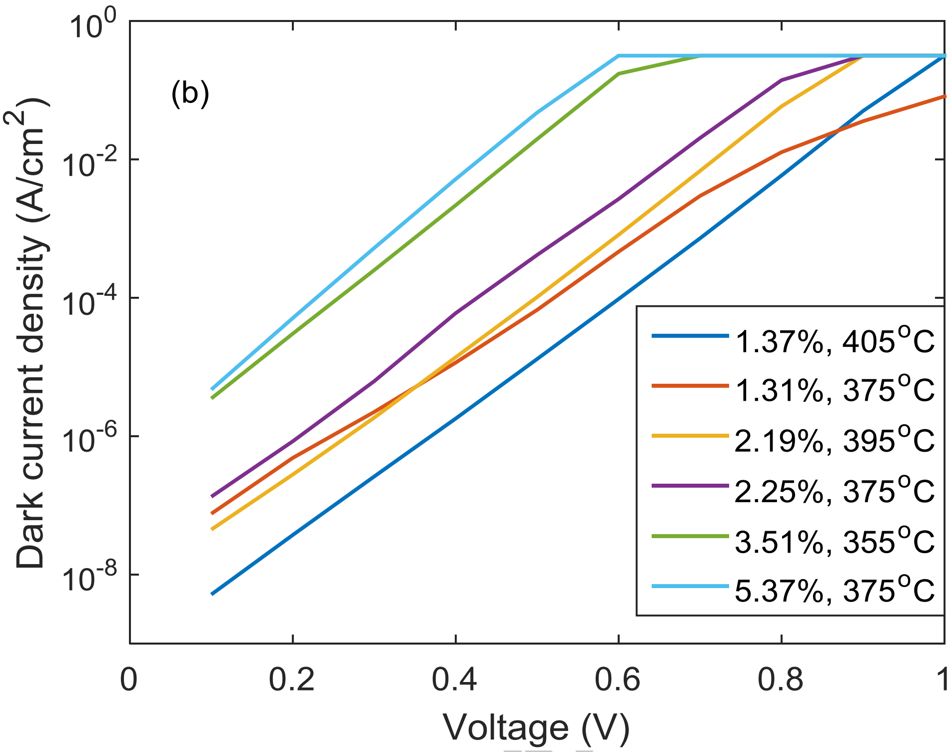


Figure 5: Dark current density for GaAsBi diodes under (a) reverse bias, and (b) forward bias, not all devices are shown here for simplicity

Many devices were tested on each wafer, and the one with the lowest dark currents was selected for analysis. This was based on the rationale that there are several factors during growth and fabrication which could lead to a degradation of the device performance, but nothing that could improve the device performance relative to others on the same wafer. Regardless, in most cases the forward dark currents show a good agreement between devices on the same epilayer, and scale with area. The only exception was the device grown at 385 °C which has a factor of 2 difference between the different size devices in forward bias.

From figure 5(b), the devices all exhibit diode-like behaviour in forward bias, with ideality factors close to 2. At high bias the dark current density of some of the devices is limited by a high series resistance between the metal and the semiconductor. It is apparent that an increased growth temperature results in a lower dark current density for the same Bi content. An increased Bi content also results in a higher dark current density.

From figure 5(a) there is weak correlation between the bismuth content and the dark current density in reverse bias. There is more variation between devices on the same wafer in reverse bias than in forward bias, and not all the devices scale with area. In addition, several of the epilayers show a changing gradient in the dark current density, meaning that the dominant generation-recombination process is changing as a function of bias. Low resistance paths, possibly at the edge of the mesa structure, likely have a large impact on the dark current in reverse bias.

The reverse saturation current density (J_{sat}) of strained pin diodes was found to be related to the dislocation density [26], and is used here as a figure of merit for the performance of the diodes. The reverse saturation current was calculated from the forward bias data using the Shockley diode equation, and plotted against Bi content in figure 6.

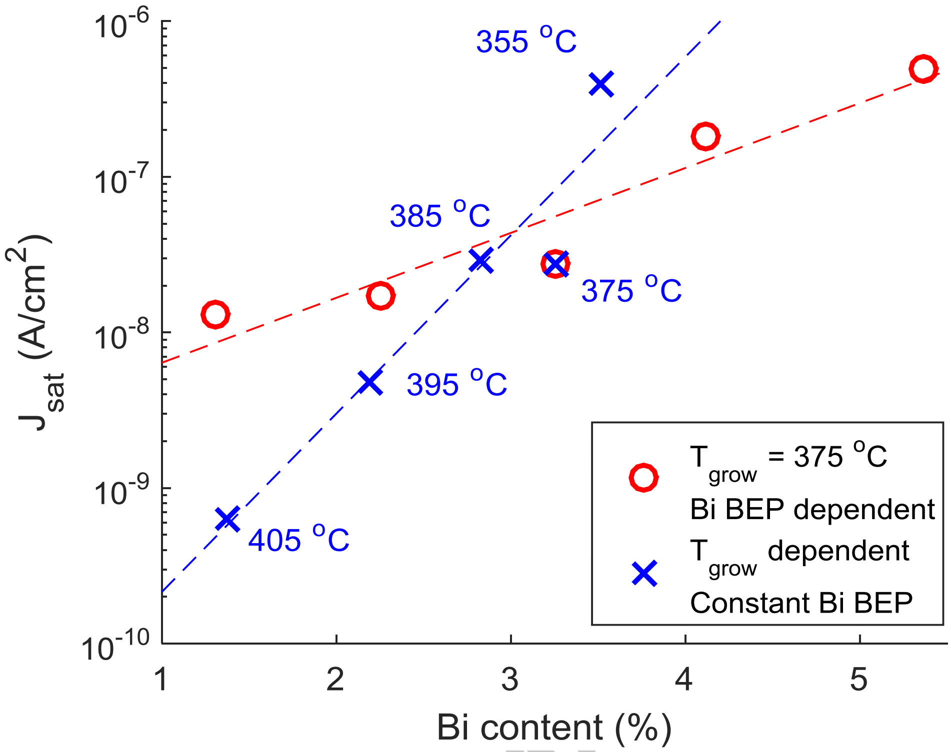


Figure 6: Reverse saturation current density of GaAsBi diodes calculated from the Shockley diode equation and forward bias data, as a function of Bi content. The annotations denote the growth temperature of the devices

From figure 6, increasing the Bi flux (circles) results in an exponential increase in J_{sat}. However, the incorporation of more bismuth by lowering the growth temperature (crosses) increases J_{sat} at a faster rate, implying that growth temperature related defects have a greater impact than Bi related defects on the dark current of the device. It is likely that the minority carrier lifetime is reduced for the diodes grown at lower temperatures due to a higher rate of defect-assisted recombination. This is evidence that GaAsBi opto-electronic devices should be grown at the highest possible temperature.

Capacitance-voltage (CV) measurements (not shown here) indicate that the depletion widths at zero bias are between 100 and 115 nm, which suggests that the i-regions of the devices (95-106 nm, including the GaAs spacer) are fully depleted. This means that the built in voltage cannot be accurately determined from the CV data.

Photoresponsivity

The photo-responsivity of the devices was measured under zero bias, and converted to external quantum efficiency (EQE) data - see figure 7.

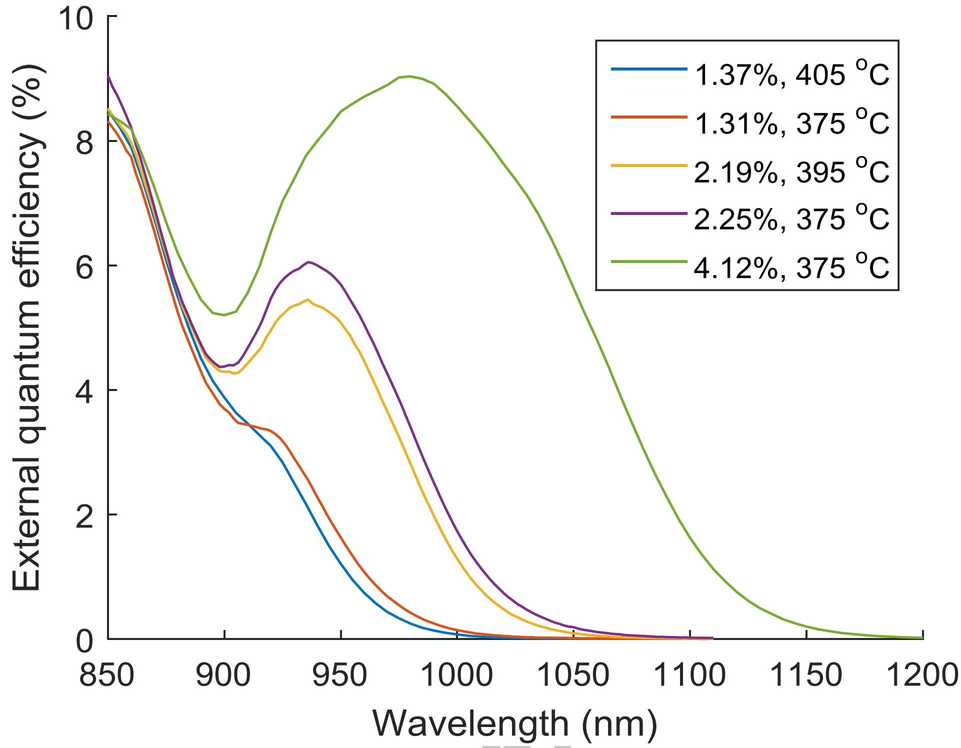


Figure 7: EQE of GaAsBi diodes under zero bias, the Bi content and growth temperature of each device is shown in the legend

From figure 7, the devices show a peak in the EQE due to photo-current generated in the i-region. The two pairs of devices with a comparable Bi content have a similar photo-response, after considering the experimental error (±10% relative). Since the i-region is only around 90 nm thick in all devices, the electric field is high enough to sweep the photo-generated carriers out of the depletion region before significant trap-assisted recombination can occur. The growth of a similar set of diodes with thicker i-regions would allow a more in-depth analysis of how the EQE relates to the growth conditions.

Discussion

The PL and JV measurements are in agreement that growth temperature related defects have a greater impact than bismuth related defects on the total defect density. The degradation of the structural properties when growing at higher temperatures could have implications for the growth of GaAsBi devices such as lasers. However, it is possible that a better understanding of the function of the bismuth pre-layer and its effect on the Bi incorporation profile can alleviate this issue.

Conclusions

A series of GaAsBi pin diodes were grown using MBE. Two pairs of diodes contain a similar Bi content despite being grown under different conditions. This allows the influence of the growth temperature and Bi content on the device properties to be independently studied. XRD results suggest that the GaAsBi layer uniformity is degraded for growth at high temperatures, however PL measurements show that higher temperature growth produces epilayers with more intense emissions. Current-voltage measurements show that both the Bi content and the growth temperature influence the dark current density, but the growth temperature has a larger effect. This suggests that GaAsBi opto-electronic devices should be grown at the highest temperature possible for the desired Bi content.

Further measurements are needed to identify the Bi incorporation profile and the type of defects that are present in the GaAsBi layers.

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References

[1] K. Alberi et al, Applied Physics Letters **91**, 051909, 2007, doi: 10.1063/1.2768312
[2] S.J. Sweeney and S.R. Jin, J. Appl. Phys. **113**, 043110, 2013, doi: 10.1063/1.4789624
[3] R.D. Richards et al, Journal of Crystal Growth **425**, 237-240, 2015, doi: 10.1016/j.jcrysgro.2015.02.053
[4] T. Thomas et al, Semicond. Sci. Technol. **30**, 094019, 2015, doi: 10.1088/0268-1242/30/9/094010
[5] C.J. Hunter et al, Photonics Technology Letters **24**, 2191-2194, 2012, doi: 10.1109/LPT.2012.2225420
[6] P. Ludewig et al, Applied Physics Letters **102**, 242115, 2013, doi: 10.1063/1.4811736
[7] R.A. Simmons et al, Applied Physics Letters **107**, 142401, 2015, doi: 10.1063/1.4932122
[8] R.B. Lewis et al, Appl. Phys. Lett. **101**, 082112, 2012, doi: 10.1063/1.4748172
[9] S. Tixier et al, Applied Physics Letters **82**, 14, 2003, doi: 10.1063/1.1565499
[10] W. Bennarndt et al, Journal of Crystal Growth **436**, 56-61, 2016, doi: 10.1016/j.jcrysgro.2015.11.021
[11] A.R. Mohmad et al, Micro and Nanoelectronics (RSM), 2015 IEEE Regional Symposium Conference Proceedings, 19-21 August 2015, doi: 10.1109/RSM.2015.7355020
[12] A.J. Ptak et al, Journal of Crystal Growth **338**, 107-110, 2012, doi: 10.1016/j.jcrysgro.2011.10.040
[13] V. Bahrami-Yekta et al, Semicond. Sci. Technol. **30**, 094007, 2015, doi: 10.1088/0268-1242/30/9/094007
[14] P. M. Mooney et al, Semicond. Sci. Technol. **31**, 6, 2016, doi:10.1088/0268-1242/31/6/065007
[15] D.A. Beaton et al, Journal of Applied Physics **118**, 235701, 2015, doi: 10.1063/1.4937574
[16] J.H. Neave et al, Surface Science **133**, 267-278, 1983, doi: 10.1016/0039-6028(83)90495-8
[17] F. Bastiman et al, Journal of Crystal Growth **341**, 1, 19-23, 2012, doi: 10.1016/j.jcrysgro.2011.12.058
[18] D.F. Reyes et al, Nanoscale Res. Lett. **9**, 23, 2014, doi: 10.1186/1556-276X-9-23
[19] R.D. Richards et al, Journal of Crystal Growth **390**, 120-124, 2014, doi: 10.1016/j.jcrysgro.2013.12.008
[20] A.R. Mohmad et al, Physica Status Solidi (B) Basic Research **251**, 6, 1276-1281, 2014, doi: 10.1002/pssb.201350311
[21] K. Oe, Jpn. J. Appl. Phys **41**, 2801-2806, 2002, doi: 10.1143/JJAP.41.2801
[22] X. Lu et al, Applied Physics Letters **95**, 041903, 2009, doi: 10.1063/1.3191675
[23] A.R. Mohmad et al, Applied Physics Letters **99**, 042107, 2011, doi: 10.1063/1.3617461
[24] D. Dagnelund et al, Applied Physics Letters **104**, 052110, 2014, doi: 10.1063/1.4864644
[25] G. Vardar et al, Applied Physics Letters **102**, 042106, 2013, doi: 10.1063/1.4789369
[26] J.P.R. David et al, Applied Physics Letters **67**, 7, 1995, doi: 10.1063/1.114690