

Telecommunication wavelength GaAsBi light emitting diodes

ISSN 1751-8768
 Received on 2nd June 2015
 Revised on 20th July 2015
 Accepted on 30th July 2015
 doi: 10.1049/iet-opt.2015.0051
 www.ietdl.org

Robert Douglas Richards¹ ✉, Christopher Jack Hunter¹, Faebian Bastiman¹,
 Abdul Rahman Mohamad^{1,2}, John Paul R. David¹

¹Department of Electronic and Electrical Engineering, University of Sheffield, Sheffield, UK

²Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

✉ E-mail: r.richards@sheffield.ac.uk

Abstract: GaAsBi light emitting diodes containing ~6% Bi are grown on GaAs substrates. Good room-temperature electroluminescence spectra are obtained at current densities as low as 8 Acm^{-2} . Measurements of the integrated emitted luminescence suggest that there is a continuum of localised Bi states extending up to 75 meV into the bandgap, which is in good agreement with previous photoluminescence studies. X-ray diffraction analysis shows that strain relaxation has probably occurred in the thicker samples grown in this study.

1 Introduction

Over the past decade there has been interest in incorporating bismuth into conventional III–V compounds. GaAsBi is the most common of these; however, more recently, other compounds such as InAsBi [1], InGaAsBi [2, 3], InPBi [4], and GaSbBi [5] have been reported. Incorporating bismuth leads to a reduction in the bandgap of the alloy and also increases the spin-orbit splitting energy of the alloy, which offers the potential to reduce Auger recombination in lasers when $E_{\text{SO}} > E_{\text{g}}$ [6]. This has been shown to occur for Bi concentrations above 10% [7] in GaAsBi.

Light emitting diodes (LEDs) containing GaAsBi active regions have previously been grown by molecular beam epitaxy (MBE) [8]. The bismuth content was 1.8% and room-temperature emission from the GaAsBi layer was observed at a wavelength of 987 nm. Pressure-dependent measurements on similar samples showed evidence of carrier leakage into the GaAs barriers and also suggested that the GaAsBi/GaAs heterojunction is type I [9]. More recently, a single quantum well GaAsBi/(Al)GaAs laser operating under electrical injection has been grown by metal-organic vapour phase epitaxy (MOVPE) [10].

For communications applications, lasers/LEDs operating at 1.3 or 1.55 μm are desirable. To fully understand such devices, the bulk luminescence properties of GaAsBi (without the quantum effects produced by quantum wells or dots) must be investigated. In this paper, we characterise p–i–n diode structures, containing bulk GaAsBi layers with ~6% Bi, which act as LEDs operating at about 1.2 μm .

2 Experimental methods

All samples were grown on an Omicron MBE-scanning tunnelling microscopy (MBE-STM) system. The MBE chamber is fitted with effusion cells for Al, Ga, In, and Bi, as well as a Be/Si dual dopant cell. The growth of the samples analysed during this work is described elsewhere [11]. Fig. 1 shows the structures diagrammatically. The thin GaAs spacer layers were included in an attempt to allow the Bi on the growing surface to desorb, preventing the formation of Bi droplets. For electrical characterisation, the samples were fabricated into 200 μm radius mesa diodes using standard fabrication techniques.

Small sections of each sample were mounted on TO5 headers in order to carry out electroluminescence measurements. The electroluminescence (EL) from the samples was dispersed by a

monochromator and detected using a liquid-nitrogen cooled germanium detector. Low-temperature measurements were carried out in a cryostat which was cooled by a closed-cycle helium compressor.

The ω – 2θ X-ray diffraction (XRD) measurements throughout this work were taken on a Bruker D8 Discover XRD machine using $\text{Cu } \alpha_1$ radiation.

3 Results and discussion

3.1 Initial sample characterisation

The initial room-temperature EL spectra taken from all three diodes are shown in Fig. 1. As the GaAsBi region thickness is increased from 100 to 200 nm, there is a reduction of 40% in the peak EL intensity. This is consistent with a doubling of the number of defects per unit area as the GaAsBi region thickness is doubled. However, when the GaAsBi region thickness is increased to 350 nm (a further factor of 1.75), the peak EL intensity is reduced by 85%. This dramatic reduction in EL intensity suggests that R7 has seen a significant increase in non-radiative processes and may indicate that it has undergone significant strain relaxation.

Further evidence for this is shown in the symmetric 004 XRD spectra, previously published in [11] and shown in Fig. 2. The spectra show a tensile peak next to the substrate that becomes increasingly prominent with increasing GaAsBi thickness. This suggests that as the GaAsBi layer thickness is increased, it becomes increasingly strain relaxed; the upper GaAs cladding layers are then grown in tensile strain on top of this layer.

Owing to the weak EL signal from R7, the remaining discussion focuses solely on R2 and R4.

3.2 Room-temperature electroluminescence

Room-temperature EL spectra taken from both samples as a function of injection current are shown in Fig. 3. The peak emission wavelength was about 1.2 μm in both cases, suggesting a Bi content of ~6% in both samples. Emission was observed at injection current densities as low as 8 Acm^{-2} , which is lower than the lowest injection current density used by Lewis *et al.* [8] (50 Acm^{-2}) or by Hossain *et al.* [9] (25 Acm^{-2}) on similar diodes. In these spectra, a peak at ~880 nm is observed, which is probably emission from the GaAs cladding layers. Emission around this

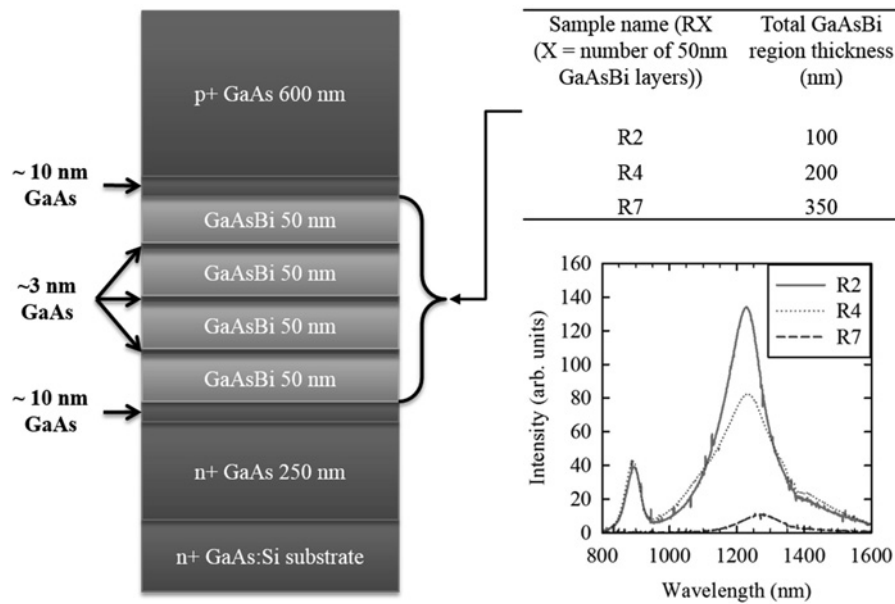


Fig. 1 Sample structures grown during this work (the structure pictured is that of R4). Also shown are the room-temperature EL spectra of the diodes, using injection currents of 80 Acm^{-2}

wavelength was also observed in the electroluminescence spectra of the LEDs in [8]; pressure-dependent measurements performed on similar samples [9] also showed the presence of carrier leakage into the GaAs cladding.

3.3 Low-temperature electroluminescence

EL measurements were also carried out at 20 K using a range of injection currents. The spectra from R2 and R4 are shown in Fig. 4. The spectra have an asymmetric shape, and the peaks blue-shift slightly with increasing injection current ($\sim 25 \text{ meV}$ for an order of magnitude change in current). This behaviour can be explained by the presence of disorder and Bi clustering, which give rise to localised states within the bandgap [12, 13]. At low temperatures, holes fall into these states and do not have sufficient thermal energy to escape, leading to the formation of localised excitons. The energy of the luminescence peak is thus less than the bandgap energy. As the carrier density (in this case, the injection current) increases, the localised states become filled and the luminescence peak shifts to higher energies [12–15].

The spectra all show a low energy, exponential tail. Low-energy tails in luminescence spectra have been observed for GaAsBi [16, 17], and also for other disordered materials such as (In)GaAsN

[18]. They are attributed to recombination of excitons trapped in localised states within the bandgap. In dilute nitrides these states are close to the conduction band, whereas for bismides, they are close to the valence band.

The low-temperature spectra shown in Fig. 4 show a significantly attenuated GaAs peak. This suggests that the GaAs peak is thermally activated; it is possibly due to carriers escaping from the GaAsBi and recombining in the GaAs cladding layers. The small conduction band offsets in GaAsBi would suggest that the escaping carriers are electrons.

3.4 Integrated emitted luminescence

The dominant carrier recombination mechanisms in the GaAsBi layers were analysed by recording the integrated emitted luminescence (IEL) as a function of injection current, j_{inject} . Following the analysis used in [19], when the IEL is plotted against j_{inject} on a log–log plot, the gradient should vary between 1 and 2, where a value of 1 shows that radiative recombination is dominant and a value of 2 shows that non-radiative recombination is dominant. An intermediate value shows that both processes are contributing.

The results are shown in Fig. 5. The gradient is 1 at low temperature (20 K) and 2 at room temperature for both samples. This suggests that radiative recombination is dominant at low temperature, but non-radiative recombination is dominant at room temperature. Similar behaviour has been observed for photoluminescence from GaAsBi layers with $[\text{Bi}] = 3\%$ [14]. In Fig. 5a, there is a reduction in the gradient of both curves at high injection current; this is probably due to sample heating. If the low-temperature EL is dominated by radiative processes, then a rough estimate of the radiative efficiency of the material at room temperature can be obtained by dividing the room-temperature luminescence by the low-temperature luminescence. In this case, at room temperature, the radiative efficiencies are 2.3 and 3.3% for R2 and R4, respectively.

By plotting the log of the IEL against $1000/T$, it is possible to extract the activation energy of the carriers in each sample. These plots are shown in Fig. 6.

It is clear that there is more than one activation energy for each diode. The data in Fig. 6 have been fitted with several different activation energies, each one determined by using a least-squares fit to the data in a given temperature range. However, the data

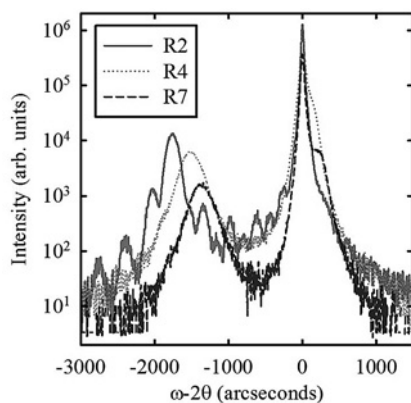


Fig. 2 004 XRD spectra from the diodes grown in this work. Data previously published in [11]

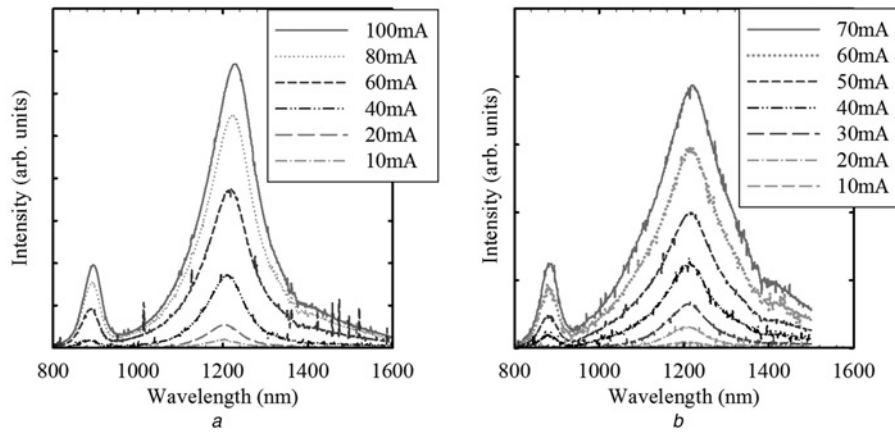


Fig. 3 Room-temperature electroluminescence

a Sample R2
b Sample R4

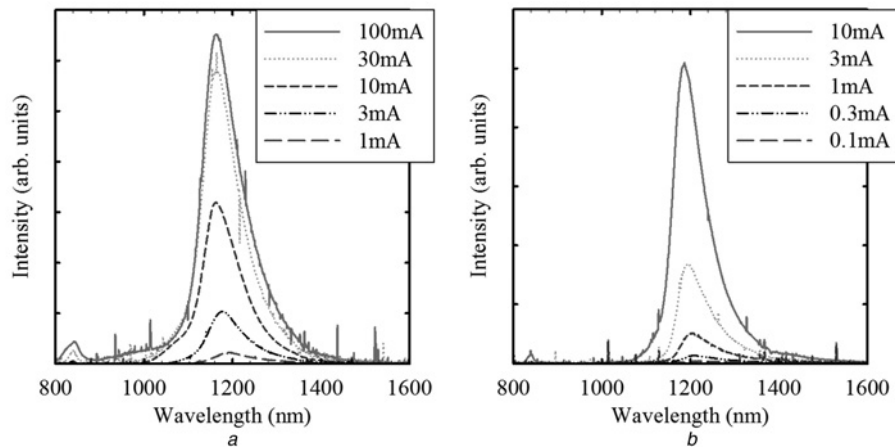


Fig. 4 Low-temperature electroluminescence

a Sample R2
b Sample R4

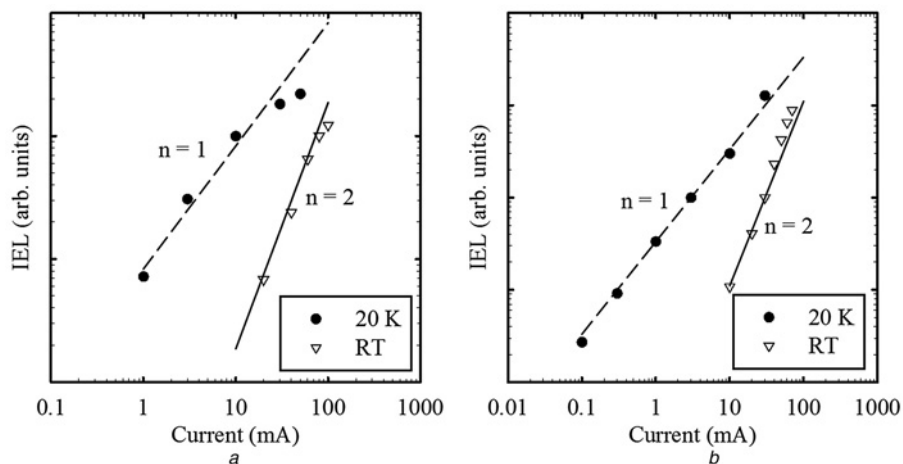


Fig. 5 Log-log plots of IEL as a function of injection current at room temperature and at 20 K

a Sample R2
b Sample R4

could have been adequately fit using several different combinations of activation energies at different temperatures. It seems likely, therefore, that there is no single, well-defined energy level in these

diodes. The largest activation energy used in this fitting is 75 meV. It is probable that these activation energies arise from the presence of localised energy levels in the bandgap caused by the

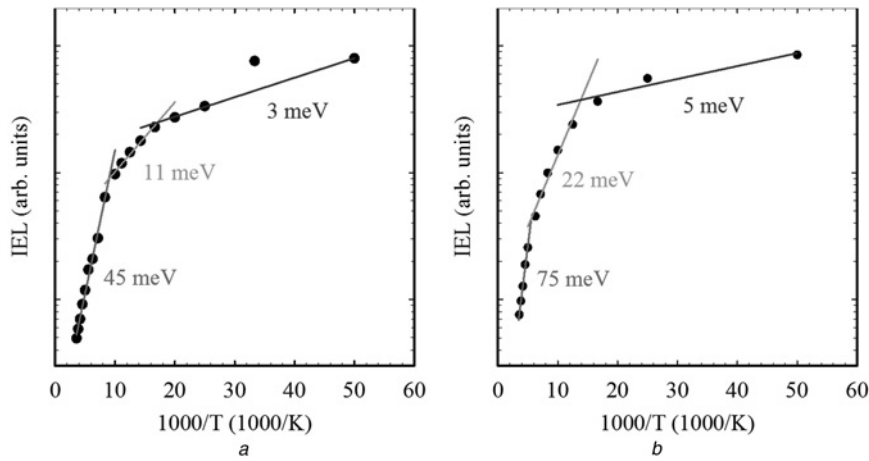


Fig. 6 Activation energies extracted from the temperature dependence of the IEL of each sample

a Sample R2
b Sample R4

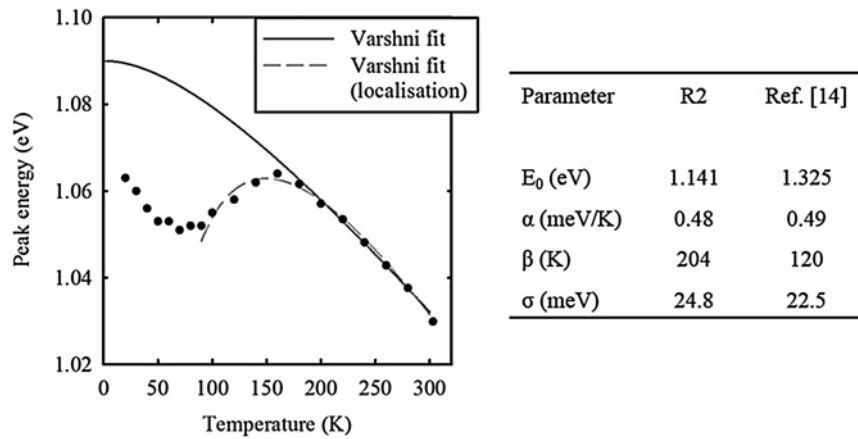


Fig. 7 Peak EL energy of sample R2 as a function of temperature

clustering of Bi atoms. This result suggests that there is a continuous range of Bi-induced localised states that extend up to 75 meV into the bandgap, which is consistent with the findings of Yoshimoto *et al.* [20].

3.5 Temperature-dependent luminescence

The temperature dependence of the peak energy of the luminescence from GaAsBi samples has previously been observed to follow an ‘S-shaped’ dependence [13–15]. This ‘S-shape’ can be explained with reference to localised states within the bandgap, as described in [21]. The Varshni equation is shown in (1) [22]

$$E_g(T) = E_0 - \frac{\alpha T^2}{(T + \beta)} \quad (1)$$

where E_g is the bandgap at temperature T ; E_0 is the bandgap at 0 K; α and β are fitting parameters. For semiconductors that contain localised states within the bandgap, the equation is modified, as shown in (2) [23]

$$E_g(T) = E_0 - \frac{\alpha T^2}{(T + \beta)} - \frac{\sigma^2}{k_B T} \quad (2)$$

where σ is a parameter that indicates the degree of localisation within the structure and k_B is Boltzmann’s constant.

The temperature dependence of the main EL peak from R2 is shown in Fig. 7, along with fits to the data using the standard and modified Varshni equations ((1) and (2), respectively). Also shown are the fitting parameters for R2, compared with the values found in [14] from a photoluminescence investigation of a GaAsBi sample with ~3% Bi.

The main peak appears to follow an S-shaped temperature dependence. This is in contrast to the EL results in [8] where the GaAsBi peak was observed to follow the conventional Varshni equation. The lower E_0 value for R2 compared with that in [14] is expected due to the higher Bi content of the samples in this work. The α values are similar and are both less than the value reported for a GaAs control sample in [14] (0.56 meV/K). This confirms that incorporating Bi reduces the temperature dependence of the bandgap.

4 Conclusions

GaAsBi LEDs were grown on GaAs substrates. The LEDs showed good room-temperature EL at about 1.20 μm , indicating a Bi content of about 6%. This is consistent with the previous work on these devices [11]. Reasonable EL spectra were obtained from these devices at a current density of 8 Acm^{-2} , which is considerably lower than the lowest current densities used in previous studies by other groups [8]. The temperature dependence of the IEL from these devices suggests that radiative recombination mechanisms dominate at 20 K, and non-radiative recombination dominates at room temperature. A temperature-dependent IEL

investigation of these samples shows that there is probably a continuous distribution of Bi-induced localised states that extend up to 75 meV into the bandgap.

5 References

- 1 Svensson, S.P., Hier, H., Sarney, W.L., *et al.*: 'Molecular beam epitaxy control and photoluminescence properties of InAsBi', *J. Vac. Sci. Technol. B*, 2012, **30**, (2), p. 02B109
- 2 Feng, G., Oe, K., Yoshimoto, M.: 'Bismuth containing III-V quaternary alloy InGaAsBi grown by MBE', *Phys. Status Solidi A*, 2006, **203**, (11), pp. 2670–2673
- 3 Zhong, Y., Dongmo, P.B., Petropoulos, J.P., *et al.*: 'Effects of molecular beam epitaxy growth conditions on composition and optical properties of $\text{In}_x\text{Ga}_{1-x}\text{Bi}_y\text{As}_{1-y}$ ', *Appl. Phys. Lett.*, 2012, **100**, (11), p. 112110
- 4 Gu, Y., Wang, K., Zhou, H., *et al.*: 'Structural and optical characterizations of InPBi thin films grown by molecular beam epitaxy', *Nanoscale Res. Lett.*, 2014, **9**, (1), p. 24
- 5 Rajpalke, M.K., Linhart, W.M., Birkett, M., *et al.*: 'Growth and properties of GaSbBi alloys', *Appl. Phys. Lett.*, 2013, **103**, (14), p. 142106
- 6 Broderick, C.A., Usman, M., Sweeney, S.J., *et al.*: 'Band engineering in dilute nitride and bismide semiconductor lasers', *Semicond. Sci. Technol.*, 2012, **27**, (9), p. 094011
- 7 Batool, Z., Hild, K., Hosea, T.J.C., *et al.*: 'The electronic band structure of GaBiAs/GaAs layers: influence of strain and band anti-crossing', *J. Appl. Phys.*, 2012, **111**, (11), p. 113108
- 8 Lewis, R.B., Beaton, D.A., Lu, X., *et al.*: 'GaAs $_{1-x}$ Bi $_x$ light emitting diodes', *J. Cryst. Growth*, 2009, **311**, (7), pp. 1872–1875
- 9 Hossain, N., Marko, I.P., Jin, S.R., *et al.*: 'Recombination mechanisms and band alignment of GaAs $_{1-x}$ Bi $_x$ /GaAs light emitting diodes', *Appl. Phys. Lett.*, 2012, **100**, (5), p. 051105
- 10 Ludewig, P., Knaub, N., Hossain, N., *et al.*: 'Electrical injection Ga(AsBi)/(AlGa)As single quantum well laser', *Appl. Phys. Lett.*, 2013, **102**, (24), p. 242115
- 11 Hunter, C.J., Bastiman, F., Mohmad, A.R., *et al.*: 'Absorption characteristics of GaAs $_{1-x}$ Bi $_x$ /GaAs diodes in the near-infrared', *IEEE Photonics Technol. Lett.*, 2012, **24**, (23), pp. 2191–2194
- 12 Imhof, S., Thranhardt, A., Chernikov, A., *et al.*: 'Clustering effects in Ga(AsBi)', *Appl. Phys. Lett.*, 2010, **96**, (13), p. 131115
- 13 Mohmad, A.R., Bastiman, F., Hunter, C.J., *et al.*: 'Localization effects and band gap of GaAsBi alloys', *Phys. Status Solidi B*, 2014, **251**, (6), pp. 1276–1281
- 14 Mohmad, A.R., Bastiman, F., Ng, J.S., *et al.*: 'Photoluminescence investigation of high quality GaAs $_{1-x}$ Bi $_x$ on GaAs', *Appl. Phys. Lett.*, 2011, **98**, (12), p. 122107
- 15 Yoshimoto, M., Itoh, M., Tominaga, Y., *et al.*: 'Quantitative estimation of density of Bi-induced localized states in GaAs $_{1-x}$ Bi $_x$ grown by molecular beam epitaxy', *J. Cryst. Growth*, 2013, **378**, pp. 73–76
- 16 Mazur, Y.I., Dorogan, V.G., Benamara, M., *et al.*: 'Effects of spatial confinement and layer disorder in photoluminescence of GaAs $_{1-x}$ Bi $_x$ /GaAs heterostructures', *J. Phys. D, Appl. Phys.*, 2013, **46**, (6), p. 065306
- 17 Mazur, Y.I., Dorogan, V.G., Schmidbauer, M., *et al.*: 'Strong excitation intensity dependence of the photoluminescence line shape in GaAs $_{1-x}$ Bi $_x$ single quantum well samples', *J. Appl. Phys.*, 2013, **113**, (14), p. 144308
- 18 Buyanova, I.A., Chen, W.M., Pozina, G., *et al.*: 'Optical properties of GaNAs/GaAs structures', *Mater. Sci. Eng. B*, 2001, **82**, (1–3), pp. 143–147
- 19 Hasbullah, N.F., Ng, J.S., Liu, H.Y., *et al.*: 'Dependence of the electroluminescence on the spacer layer growth temperature of multilayer quantum-dot laser structures', *IEEE J. Quantum Electron.*, 2009, **45**, (1), pp. 79–85
- 20 Yoshimoto, M., Itoh, M., Tominaga, Y., *et al.*: 'Quantitative estimation of density of Bi-induced localized states in GaAs $_{1-x}$ Bi $_x$ grown by molecular beam epitaxy', *J. Cryst. Growth*, 2013, **378**, pp. 73–76
- 21 Potter, R.J., Balkan, N.: 'Optical properties of GaNAs and GaInAsN quantum wells', *J. Phys., Condens. Matter*, 2004, **16**, (31), p. S3387
- 22 Varshni, Y.P.: 'Temperature dependence of the energy gap in semiconductors', *Physica*, 1967, **34**, (1), pp. 149–154
- 23 Eliseev, P.G., Perlin, P., Lee, J., *et al.*: 'Blue' temperature-induced shift and band-tail emission in InGaN-based light sources', *Appl. Phys. Lett.*, 1997, **71**, (5), pp. 569–571