Band engineering in dilute nitride and bismide semiconductor lasers

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Abstract

Highly mismatched semiconductor alloys such as GaN\textsubscript{x}As\textsubscript{1-x} and GaBi\textsubscript{x}As\textsubscript{1-x} have several novel electronic properties, including a rapid reduction in energy gap with increasing \textit{x} and also, for GaBiAs, a strong increase in spin-orbit-splitting energy with increasing Bi composition. We review here the electronic structure of such alloys and their consequences for ideal lasers. We then describe the substantial progress made in the demonstration of actual GaInNAs telecommunication (telecom) lasers. These have characteristics comparable to conventional InP-based devices. This includes a strong Auger contribution to the threshold current. We show, however, that the large spin-orbit-splitting energy in GaBiAs and GaBiNAs could lead to the suppression of the dominant Auger recombination loss mechanism, finally opening the route to efficient temperature-stable telecom and longer wavelength lasers with significantly reduced power consumption.

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

1. Introduction

The exponential growth in optical telecommunications and the internet has been underpinned by the development of semiconductor lasers emitting at 1.3 and at 1.55 μm, the wavelengths at which, respectively, dispersion is zero and losses are minimised in standard optical fibres [1, 2]. The lasers designed to operate at these wavelengths are based primarily on the growth of quaternary InGaAsP and InGaAlAs alloy structures on InP substrates. Despite their widespread application, there are several significant drawbacks associated with these devices, mostly associated with the constraints of growing on InP substrates. The development of telecom lasers grown on GaAs substrates could bring several advantages. Firstly, because GaAs is a more robust material, growth can be carried out on larger substrates. Secondly, better optical confinement can be achieved in GaAs heterostructures, because of the larger refractive index difference between GaAs and AlGaAs compared to that between InP and the quaternary alloys. Vertical cavity surface emitting lasers can therefore be grown monolithically on GaAs, but only with great difficulty on InP. In addition, because AlGaAs has a considerably larger energy gap than InP and can be grown lattice-matched on GaAs, it should be possible to achieve much better electrical confinement in a telecom laser based on GaAs. A further issue with 1.3 and 1.55 μm semiconductor lasers is that their threshold current and the optical cavity losses tend to increase strongly with increasing temperature, due largely to a combination of two intrinsic loss mechanisms, Auger recombination [3–5] and intervalence band absorption (IVBA) [6]. Telecom lasers then need to be operated on a thermo-electric cooler for many applications, significantly increasing the overall energy budget associated with their operation.

Considerable advantage could therefore be gained if high quality and reliable telecom lasers could be developed on GaAs. This is very difficult to achieve using conventional quantum well (QW) structures. Highly efficient lasers using strained InGaAs QW structures are very well established for emission around 1 μm, but too much In is needed and there is therefore too large a lattice mismatch relative to GaAs to achieve reliable lasers emitting at 1.3 μm and beyond [7]. There was therefore considerable interest generated when it was shown that replacing a small fraction of As atoms by N in Ga(In)As leads to a rapid reduction in energy gap, with the
gap decreasing by about 150 meV for \( x = 1\% \) in GaIn\(_x\)As\(_{1-x}\) [8, 9]. This opens the possibility to achieve longer wavelength emission on a GaAs substrate, supporting the demonstration of 1.3 \( \mu \)m edge-emitting and vertical cavity lasers [10–12], as well as 1.5 \( \mu \)m edge-emitting devices [13, 14].

The electronic structure of dilute nitride alloys is of considerable interest from a theoretical perspective, both to understand the origins of the rapid reduction in energy gap and also to understand the consequences of that reduction for laser action. It is well established that replacing a single As atom by N in GaAs introduces a resonant defect state above the conduction band (CB) edge [15]. A major breakthrough was achieved for dilute nitride alloys with the demonstration by Walukiewicz and co-workers that the reduction in energy gap in Ga(In)N\(_x\)As\(_{1-x}\) is due to a band-anticrossing interaction (BAC) between the CB edge and higher-lying localized nitrogen resonant states [16].

Given the significant differences in the CB structure of GaInNAs compared to conventional III–V semiconductors, it is important to elucidate the influence of N not only on the electronic structure but also on the gain characteristics of ideal dilute nitride lasers. We have shown [17, 18] and describe below that the incorporation of N degrades properties such as differential gain compared to that of the best GaInAs/GaAs structures. Nevertheless, the overall characteristics of an ideal GaInNAs/GaAs laser are still expected to be at least as good as those of conventional InP-based telecom lasers.

Having established the characteristics of ideal structures, we then turn to consider actual GaInNAs lasers operating in the telecom wavelength band between 1.3 and 1.5 \( \mu \)m. We have shown experimentally that the threshold current of GaInNAs lasers is dominated by non-radiative recombination processes, including both defect-related and Auger recombination [19]. Theoretical calculations [20] and experimental analysis [19] show that Auger recombination is a major loss mechanism in GaInNAs- and InP-based 1.3 and 1.5 \( \mu \)m lasers. In the dominant CHSH Auger process, a Conduction electron and a Heavy hole (HH) recombine across the energy gap but, instead of emitting a photon, they excite into the Spin-split-off band a Hole from near the valence band (VB) maximum [4].

CHSH Auger recombination is the dominant intrinsic loss mechanism that ultimately limits all current telecom lasers. Because Auger recombination involves three carriers, its contribution to the threshold current density increases (using the Boltzmann approximation) as \( n_{th}^3 \), where \( n_{th} \) is the threshold carrier density. The rapid increase of \( n_{th}^3 \) with temperature then explains the strong temperature sensitivity of the threshold current in semiconductor diode lasers at telecom and longer wavelengths. In addition to Auger recombination, IVBA also degrades laser performance. In the IVBA process, a photon is re-absorbed by an electron in the spin-split-off band which is excited to an empty (hole) state near the top of the VB. Like the CHSH Auger process, IVBA is therefore also sensitive to the spin-split-off energy. IVBA causes \( n_{th} \) to increase superlinearly with temperature [21], further exacerbating Auger recombination and additionally degrading the differential quantum efficiency above threshold. The combination of Auger recombination and IVBA causes the output power of telecom lasers to be strongly temperature sensitive over the typical operating temperature range [22].

It would therefore be highly beneficial if these loss mechanisms could be eliminated from telecom lasers. This cannot be achieved using conventional III–V alloys based on (GaAlIn)(NPAsSb), where the energy gap \( E_g \) always exceeds the spin-orbit-splitting energy \( \Delta SO \) in materials that emit at 1.3 and 1.5 \( \mu \)m. It has recently been demonstrated that replacing As by Bi in GaBi\(_x\)As\(_{1-x}\) can give rise to a strong decrease in the band gap as well as a strong increase in the spin-orbit-splitting energy, leading to a \( \Delta SO > E_g \) regime in the alloy for \( x \gtrsim 10\% \) [23, 24]. Just as the introduction of N gives the possibility to engineer the CB structure, the introduction of Bi then provides an opportunity to engineer the VB structure potentially providing a route to produce telecom and longer wavelength lasers with suppressed losses [23, 25].

This review aims to provide an overview of the electronic structure of highly mismatched semiconductor alloys and of the consequences and potential benefits of such alloys for optoelectronic applications. In section 2 we present an overview of the band-anticrossing model used to describe the CB structure of dilute nitride alloys. A brief discussion of the effective masses and band offsets used in calculations on GaInNAs/GaAs material systems is given in section 3. In section 4, we discuss the effects of nitrogen incorporation on gain and loss mechanisms in ideal GaInNAs lasers, followed by a comparison between ideal and actual device behaviour. Having established through this comparison that Auger recombination remains a significant loss mechanism in all telecom lasers to date, we then present in section 5 an overview of the potential benefits of dilute bismide alloys for future, high efficiency photonic devices. Finally we summarize our conclusions in section 6.

2. Band-anticrossing model of dilute nitride CB structure

It is well-established that when a single N atom replaces an As atom in GaAs, it forms a resonant defect level above the CB edge of GaAs [15, 26]. This defect level arises because of the large difference in electronegativity and atomic size between N and As [27, 28]. A major breakthrough was achieved for dilute nitride alloys with the demonstration by Walukiewicz and co-workers using hydrostatic pressure techniques that the reduction in energy gap in Ga(In)N\(_x\)As\(_{1-x}\) is due to a BAC interaction between the CB edge and higher-lying localized nitrogen resonant states [16].

The BAC model explains the extreme band gap bowing observed in In\(_x\)Ga\(_{1-x}\)N\(_x\)As\(_{1-x}\) in terms of an interaction between two levels, one at energy \( E_c \) associated with the extended CBE state \( \psi_{c0} \) of the GaInAs matrix and the other at energy \( E_N \) associated with the localized N impurity states \( \psi_N \), with the two states linked by a matrix element \( V_{NC} \) describing the interaction between them [16]. The CB dispersion of Ga(In)N\(_x\)As\(_{1-x}\) is then given in the BAC model by the lower eigenvalue of the determinant

\[
\begin{vmatrix}
E_N - E & V_{NC} \\
V_{NC} & E_c + \frac{k_B^2 T^2}{2m_e} - E
\end{vmatrix}
\]

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\]
where \( m^* \) is an appropriately chosen CB edge effective mass for the Ga(In)As host matrix material [29]. From equation (1), the CB edge energy, \( E_{-} \), is then given by

\[
E_{-} = \frac{E_N + E_c}{2} - \sqrt{\left( \frac{E_N - E_c}{2} \right)^2 + (V_{Nc})^2}.
\]

(2)

The alloy CB edge wavefunction \( \psi_{-} \) can be found from equation (1) as \( \psi_{-} = \alpha_{\Gamma} \psi_{\alpha} + \alpha_{N} \psi_{N} \). The fractional \( \Gamma \) character of \( \psi_{-} \) is given by \( f_{\Gamma} = |\alpha_{\Gamma}|^2 \), with \( f_{\Gamma} \) then providing a useful measure of how much the N-related states in the alloy perturb the CB edge wavefunction.

A resonant feature associated with the upper eigenvalue, \( E_{+} \), has been observed in photo-reflectance (PR) measurements [16, 30, 31], appearing in GaN\(_x\)As\(_{1-x}\) for \( x \gtrsim 0.2\% \) and remaining a relatively sharp feature until \( x \sim 3\% \), beyond which composition it broadens and weakens, when the resonant state becomes degenerate with the GaAs \( L \)-related CB levels [32]. The data points in figure 1(a) show the measured variation of the \( E_{-} \) and \( E_{+} \) energy levels with N composition \( x \) at room temperature in GaN\(_x\)As\(_{1-x}\). These measured values are very well fitted using the BAC model, as illustrated by the solid lines in figure 1(a), for which we use \( E_N = 1.67 \) eV, \( E_c = 1.42 - 3.5x \) eV and \( V_{Nc} = \beta x^2 \), with \( \beta = 2.3 \) eV [33].

The BAC interaction not only reduces the energy gap but is also predicted to lead to an increased electron effective mass at the CB minimum and to a strongly nonparabolic CB dispersion. Evidence for this dispersion is provided by photo-reflectance measurements of GaNAs QW samples, where the strong band nonparabolicity is required to account for the QW excited state transition energies across a wide range of samples and as a function of hydrostatic pressure [33, 29].

Despite the wide success of the two-level BAC model, it should be acknowledged that there are several sets of experimental data which it fails to explain. For example, it significantly underestimates the electron relative effective mass, \( m^*_e \), in GaN\(_x\)As\(_{1-x}\) for \( x > 0.1\% \) [34–38]. The effective mass has been determined using a range of different techniques, with a consistent trend emerging of unexpectedly large relative mass values in GaN\(_x\)As\(_{1-x}\), such as \( m^*_e = 0.13, 0.15 \) and even 0.19 for \( x = 0.1 \) [38], 1.6 [37] and 2.0% [36], respectively.

Detailed calculations have shown that these effects arise due to the formation of N pairs and clusters in the material, which can generate defect states lying close to the CB edge of GaN\(_x\)As\(_{1-x}\) [34, 39, 40]. Hybridization between these localized states and the host matrix CB edge strongly perturbs the electronic structure, with the strength of the hybridization determined by the relative separation in energy between the N-related defect states and the CB edge [34, 39, 41].

In InAs the localized states related to N pairs and higher order complexes lie significantly above the InAs CB edge, so that replacing Ga by In to form In\(_x\)Ga\(_{1-x}\)As\(_{1-x}\) shifts the CB edge away from the N cluster state distribution [34]. This significantly reduces the effects of N cluster states on the CB edge, meaning that the BAC model has been largely successful when applied to In\(_x\)Ga\(_{1-x}\)N\(_x\)As\(_{1-x}\) alloys, accounting well for the observed BAC-like energy gaps and effective masses in these alloys [34, 41].

The electronic structure of conventional semiconductor lasers is typically analyzed using an eight-band \( k \cdot p \) model, including the CB, HH, light-hole (LH) and spin-split-off bands [42, 43]. This can be expanded to a ten-band \( k \cdot p \) model for GaInNAs, obtained by adding two additional spin-degenerate nitrogen-related states to the eight-band \( k \cdot p \) model [17, 44]. This model has provided valuable insight into the optoelectronic properties of GaInNAs alloys, having been successfully used to accurately model, for example, the measured optical transitions [33] and electron effective masses [29, 41] in GaInNAs QWs, as well as gain and loss mechanisms in 1.3 \( \mu \)m GaInNAs QW lasers [17, 19].

3. Band gap, band offsets and effective masses in GaInNAs

A range of studies have successfully interpreted the band structure of GaInNAs alloys using the BAC model. As an
How does introduction of N affect the VB offset? This is important not only to elucidate the influence of N on the electronic structure and gain characteristics of ideal dilute nitride lasers, but also to apply that understanding to the experimental analysis of GaInNAs lasers operating in the telecomm wavelength band between 1.3 and 1.5 \( \mu m \).
We present here a theoretical overview of the consequences of the electronic structure of dilute nitride alloys for laser emission. We summarize the influence of nitrogen incorporation on the calculated dipole matrix elements, electron effective mass, gain and differential gain versus carrier density and radiative current density, as well as the effect of N on the primary loss mechanisms of defect-related and Auger recombination. We then compare the theoretically estimated laser characteristics of GaInNAs-based and conventional InGaAsP-based 1.3 μm lasers.

The solid lines in figure 3(a) show the calculated band dispersion for an ideal 7 nm wide In_{0.36}Ga_{0.64}N_{0.02}As_{0.98}/GaAs QW, calculated using a ten-band kp Hamiltonian which includes the CB, HH, LH and spin-split-off (SO) states from the conventional eight-band kp model, as well as two additional spin-degenerate N-related states [17]. The dashed line shows the calculated band dispersion of the equivalent N-free 7 nm wide In_{0.36}Ga_{0.64}As/GaAs QW structure. An increased band edge effective mass and a strong nonparabolicity are clearly visible in the CB dispersion in the GaInNAs QW, due to the interaction between the lowest conduction states and the N resonant levels.

The coupling between the N level and the CB edge modifies the CB wavefunctions and reduces the interband optical transition matrix element |M_{e-h}|^2 compared to a conventional N-free alloy. Figure 3(b) shows the calculated variation as a function of in-plane wavevector k∥ for the TE and TM interband matrix elements linking the first confined electron (e1) with the first confined HH (hh1) and LH (lh1) states. The band edge, zone-centre, TE matrix element is calculated to decrease by ~30% due to the incorporation of N. The N–CB coupling therefore leads to an increased CB edge effective mass. We calculate that the band edge density-of-states effective mass in the first CB increases to 0.060m_0 in the structure with 2% N compared to a value of 0.046m_0 in the N-free case.

The reduction in |M_{e-h}|^2 and consequent increase in the CB edge effective mass, m^*_e, causes the product m^*_e × |M_{e-h}|^2 to stay approximately constant, as would be expected from kp theory: the dominant contribution to the bulk CB inverse effective mass, m^*_e × |M_{e-h}|^2, is directly proportional to |M_{e-h}|^2. The band structure and matrix elements presented in figures 3(a) and (b) were used to calculate the variation of material gain with temperature T and as a function of carrier density n and of radiative current density J_{rad}, for both an In_{0.36}Ga_{0.64}N_{0.02}As_{0.98}/GaAs QW structure and in an equivalent N-free structure [62]. The increase in the CB effective mass leads to an increase in the carrier concentration at transparency for the In_{0.36}Ga_{0.64}N_{0.02}As_{0.98}/GaAs QW laser structure and a decrease in the separation between the conduction and VB quasi-Fermi levels, $E_{F_C} - E_{F_V}$, for a fixed carrier concentration. As a consequence the peak gain decreases at a fixed carrier density in the In_{0.36}Ga_{0.64}N_{0.02}As_{0.98}/GaAs structure when compared to the N-free case, figure 4(a). There is however a much weaker variation in the peak gain versus radiative current density, figure 4(b). This weak variation reflects the fact that for a fixed quasi-Fermi level separation, the radiative current $J_{rad}$ in a QW laser is approximately proportional to $m^*_e \times |M_{e-h}|^2$, where $m^*_e$ is the band edge reduced effective mass. Because the VB mass, $m^*_v$, is always larger than the CB mass, $m^*_e$, the reduced mass $m^*_e$ is determined primarily by $m^*_e$. We saw above that $m^*_e \times |M_{e-h}|^2$ is approximately constant, thus accounting for the calculated weak variation in $J_{rad}$.

The differential gain plays a key role in determining both the threshold carrier density and the bandwidth of a directly
modulated semiconductor laser. The modulation response frequency \( \omega_t \) is proportional to the square root of the differential gain with respect to the carrier density, \( \omega_t \propto \sqrt{\frac{dg}{dn}} \). Figure 5 shows the calculated variation of differential gain at transparency and at threshold in a series of ideal 7 nm In\(_{x}\)Ga\(_{1-x}\)N\(_{y}\)As\(_{1-y}\) SQW structures. In order to maintain the QW ground-state transition energy \( \epsilon_1-\hbar\omega_1 \) constant at 0.954 eV (1.3 \( \mu \)m), we have calculated a decrease of In composition \( y \) from 55% to 30% [18]. We find that for a fixed broadening factor the calculated differential gain decreases with increasing N content, \( x \), with the most rapid decrease observed at low \( x \). As expected, the differential gain also decreases with increasing broadening factor. Because the measured broadening in GaInNAs increases with \( x \) [33], we conclude that the calculated threshold \( dg/dn \) value of \( \sim 0.86 \times 10^{-15} \) cm\(^{-1}\) for \( x = 0.02 \) is only about 40% of the value which could be achieved in an ideal GaAs 1.3 \( \mu \)m QW laser. The initial rapid decrease in differential gain (already notable at the first data point, \( x = 0.25% \)) is due to the strong coupling between the N resonant states and the CBE states, even for small values of \( x \).

Figure 4. Calculated variation of the peak material gain as a function of (a) carrier density and (b) radiative current density, in the same N-containing (solid lines) and N-free (dashed lines) SQW laser device of figures 3(a) and 3(b). ((a) and (b) reproduced from [17].)

Figure 5 suggests that the optimal GaInNAs/GaAs QW laser device should contain minimal nitrogen, ideally being N-free! This however is not possible because of the excessively large strain required to achieve 1.3 \( \mu \)m emission in a GaInAs QW. We estimated, using the strain-thickness criteria in [61], that one needs \( x > 1.5\% \) and \( y < 39\% \) to achieve 1.3 \( \mu \)m emission in a pseudomorphic In\(_{x}\)Ga\(_{1-x}\)N\(_{y}\)As\(_{1-y}\)/GaAs QW structure. The N content can be further reduced by adding more In to narrower QWs and also by growing tensile-strained layers above and below the QW, as demonstrated by Tansu et al, who achieved 1.3 \( \mu \)m emission with \( x = 0.5\% \), a QW width of 6 nm and utilising strain-compensating GaAs\(_{0.85}\)P\(_{0.15}\) tensile layers in the barrier region [63, 64].

Comparing our theoretical results on GaInNAs/GaAs with previous theoretical analysis of 1.3 \( \mu \)m InGaAsP/InP and InGaAlAs/InP structures [17, 65, 66], we find that the GaInNAs material has a higher differential gain of \( \sim 0.8 \times 10^{-15} \) cm\(^{-1}\) compared to \( \sim 0.6 \times 10^{-15} \) cm\(^{-1}\) in InP-based devices for the same amount of compressive strain (\( \sim 1.5\% \)), optical gain (\( \sim 1300 \) cm\(^{-1}\)), or well thickness (\( \sim 7 \) nm), despite the significantly larger line broadening of 18 meV assumed in GaInNAs compared to 6.6 meV in the InP-based devices. Stronger optical confinement is possible in 1.3 \( \mu \)m GaInNAs/GaAs-based lasers compared to InP-based devices, because of the larger refractive index step achievable through use of AlGaAs cladding layers. This reduces the number of QWs required in an edge-emitting device, while also opening the possibility of GaInNAs-based 1.3 and 1.5 \( \mu \)m VCSELs. The theoretical analysis presented here therefore confirms the potential of GaInNAs-based lasers both for edge- and surface-emitting laser applications in the telecommunication wavelength range.

4.2. Influence of N on loss mechanisms in GaInNAs lasers

While there has been considerable interest in the influence of nitrogen incorporation on the electronic structure and optical transitions in GaInNAs/GaAs QWs, there have been comparatively few quantitative investigations of the primary loss mechanisms in lasers based on these material systems. Such studies are of interest since they allow a direct...
comparison between the relative importance of radiative and non-radiative recombination paths in dilute nitride lasers compared to their conventional InP-based counterparts. Non-radiative recombination processes make a significant contribution to the threshold current in conventional InP-based lasers. This leads to a strong temperature dependence of the threshold current in such devices [67]. A number of factors can contribute to this temperature dependence, such as carrier leakage due to weak electron confinement [68, 69] or IVBA [6, 70], but the dominant loss mechanism in InP-based lasers at threshold is generally regarded to be Auger recombination [67, 71].

We begin our discussion of GaInNAs lasers with a description of the quantitative experimental analysis of recombination pathways in 1.3 μm GaInNAs/GaAs lasers carried out in [19], highlighting the importance of defect-related and Auger recombination in such devices. We then provide an interpretation of the observed device characteristics in terms of detailed theoretical calculations of the effects of N on Auger recombination rates in GaInNAs/GaAs systems [20]. This is then used as a basis to understand the observed threshold characteristics of GaInNAs lasers emitting across the full wavelength range from 1.2 to 1.6 μm.

Under the assumptions of charge neutrality in the active region (electron density n = hole density p) and negligible carrier leakage, the current density in a single quantum well (SQW) laser can be written in the Boltzmann approximation as

\[ J = J_{\text{mono}} + J_{\text{rad}} + J_{\text{Auger}} = e(An + Bn^2 + Cn^3) \] (3)

where \( J_{\text{mono}} \), \( J_{\text{rad}} \) and \( J_{\text{Auger}} \) refer respectively to the current densities due to monomolecular/defect-related (\( \propto n \)), radiative (\( \propto n^2 \)) and Auger (\( \propto n^3 \)) recombination, with \( A \), \( B \) and \( C \) the monomolecular, radiative and Auger recombination coefficients. In each case the recombination rate varies in the Boltzmann approximation as carrier density \( n \) to the power of the number of carriers involved—e.g. because radiative recombination is a bimolecular process, it varies as \( n^2 \).

It is possible from equation (3) to express the total current density \( J \) over a limited current range as \( J \propto n^z \), with \( 1 \leq z \leq 3 \) [3, 67] and with the value of \( z \) varying depending on whether the dominant contribution to the current density is due to monomolecular \((z = 1)\), radiative \((z = 2)\) or Auger \((z = 3)\) recombination.

It is also possible to measure the integrated spontaneous emission (SE) rate \( L \) from a semiconductor laser by etching a window in the laser substrate and then collecting the spontaneous emission emitted through the window. Because \( L \) is proportional to \( Br^2 \), this allows the total current density \( J \) to be related to the integrated spontaneous emission \( L \) as \( J \propto L^2 \), which can be rewritten as \( \ln J \propto z \ln L^2 \). This then enables \( z \) to be determined experimentally for a given laser by plotting \( \ln J \) against \( \ln L^2 \), with the slope of the log-log plot giving the value for \( z \).

Such an analysis was applied in [19] to the study of two 1.3 μm GaInNAs/GaAs laser structures, the first containing a single \( \text{In}_{0.05}\text{Ga}_{0.64}\text{N}_{0.017}\text{As}_{0.983} \) QW with GaAs barriers (SQW) and the second containing three of the same QWs but

![Figure 6. Experimentally measured variation of the monomolecular, radiative and Auger current densities at threshold, as a function of temperature for a Ga\(_{0.64}\)In\(_{0.36}\)N\(_{0.017}\)As\(_{0.983}\) SQW laser device, as determined from the analysis outlined in the text. (Reproduced from [19].)](image_url)
Auger contribution to the threshold current increases rapidly at higher temperatures, becoming the dominant current path in the given device above $T = 350$ K. This is confirmed by the measured value of $z_{th} = 2.8$ at $T = 370$ K. Comparing this to the value of $z_{th} = 2.9$ for the 1.3 μm InGaAsP/InP device of [67] shows that the GaInNAs/GaAs material system does not differ significantly in its Auger-dominated high temperature characteristics from conventional InP-based lasers.

A broadly similar behaviour was obtained in the 3QW device [19]. Increasing the number of QWs to three reduces the modal gain required per well (assuming a fixed loss level) and therefore should also reduce the threshold carrier density per well, $n_{th}$. This then reduces the relative importance of $J_{Auger}$ compared to $J_{rad}$: at the lower $n$ value, $Bn^2$ is larger compared to $Cn^3$ than it is at the higher $n_{th}$ value. However, the reduced value of $n_{th}$ simultaneously increases the relative importance of the defect-related recombination, since $An$ becomes larger compared to $Bn^2$ than at larger carrier densities. The measured value of $z_{th} = 2.4$ at $T = 370$ K in the 3QW laser is then consistent with the increased relative importance of defect-related compared to Auger recombination in this device.

The relative importance of Auger and of radiative recombination in these SQW and 3QW lasers can be explained theoretically on the basis of models employing a ten-band $k \cdot p$ Hamiltonian for GaInNAs [17, 19]. Two main Auger recombination processes are considered in telecom lasers, namely the CHSH process described earlier and the CHCC process, where a conduction electron recombines with a HH, exciting an electron from near the bottom of the CB to a higher energy CB state. Both the CHCC and CHSH processes are depicted schematically in figure 7. Previous experimental and theoretical analysis has shown that the CHSH process is dominant in conventional InP-based lasers, providing a current path which typically accounts for the majority of the Auger current [3–5].

A detailed theoretical study of the effects of N on a GaInNAs/GaAs QW structure [20] confirmed that the contribution of Auger recombination is relatively unchanged in a GaInNAs laser compared to that observed in conventional InP-based lasers. Because nitrogen incorporation in GaInNAs only perturbs the VB structure weakly, the CHSH Auger recombination mechanism, involving the excitation of a hole from the HH to the spin-split-off band, again dominates in the GaInNAs material systems, with the CHSH recombination rate in GaInNAs found to be comparable to that in the equivalent N-free system [20].

Based on this experimental [19] and theoretical [20] evidence it is clear that Auger recombination is as important in 1.3 μm GaInNAs lasers as in their InP-based counterparts. By increasing the N content, it is possible to extend the emission of GaInNAs-based lasers to longer wavelengths. The first emission beyond 1.5 μm with GaInNAs/GaAs based devices was reported in July 2000 by Fischer et al using a 5% N and 38% In double quantum well structure [72]. However, the threshold current density of these devices was very large, with $J_{th} \sim 60$ kA cm$^{-2}$ at $\lambda = 1.51$ μm. The development of GaInNAs 1.5 μm devices and the reduction in the reported threshold current was then rapid, with further improvements achieved by introducing Sb to give GaInNAsSb QW systems. The development of the GaInNAs material system was largely
driven by Infineon. In 2004 they reported long wavelength devices at \( \lambda = 1.4 \ \mu m \) with \( J_{th} = 690 \ \text{A cm}^{-2} \) and at \( \lambda = 1.43 \ \mu m \) with \( J_{th} = 1090 \ \text{A cm}^{-2} \) [73]. At the time these values were the lowest values for Sb-free devices emitting beyond 1.3 \( \mu m \). By 2005 they had extended the emission to 1.51 \( \mu m \) with a GaInNAS SQW and GaAs barriers [74]. This device had a record low threshold current density for any GaAs-based device at this wavelength with \( J_{th} = 780 \ \text{A cm}^{-2} \).

The development of the GaInNAsSb system was largely driven by the Harris group at Stanford who extended the emission wavelength to 1.55 \( \mu m \) in 2005 [75]. With further developments of their device design and optimisation of their growth the Stanford group produced devices with a record low threshold current density at 1.55 \( \mu m \) of 579 \( \text{A cm}^{-2} \) [13] using GaInNASb and GaNAS barriers in 2006. These devices remain the benchmark for 1.55 \( \mu m \) emission using the GaInNAS(Sb) material system. The Harris group led the use of antimony in the growth of GaInNAS active regions. The general consensus is that antimony acts as a reactive surfactant enhancing the incorporation of N [76]. In addition, it allows higher growth temperatures, enabling improved optical quality, because of the formation of fewer point defects [77].

McConville et al [78] in collaboration with Infineon undertook a study of threshold current density as a function of wavelength for GaInNAS/GaAs based devices. The emission wavelength of the devices spanned from 1.27 to 1.6 \( \mu m \), with this range achieved by varying the nitrogen and indium contents within the QW from 1.3% to 4.5% and from 30% to 40% respectively. Figure 8(a) shows the corresponding variation of \( J_{th} \) at room temperature as a function of wavelength. It is clear that the threshold current density increases with increasing wavelength. Using a spontaneous emission analysis similar to that described earlier, McConville quantified the contribution of each of the current paths to the threshold current density in a series of devices, as shown in figure 8(b). It is clear from figure 8(b) that the increase in threshold current is due to an increase in both the monomolecular and the Auger currents with increasing wavelength, with little change observed in the radiative current measured in the different devices. Auger recombination evidently persists over the entire wavelength range investigated.

Auger recombination places intrinsic limits on the threshold characteristics and temperature stability of GaInNAS lasers (and conventional InP-based devices) operating at telecom wavelengths. This then raises the challenge as to whether it could be possible to eliminate Auger losses and temperature sensitivity in lasers operating in the 1.3 and 1.5 \( \mu m \) wavelength ranges. To address this question, we now turn our attention to an emerging class of highly-mismatched III–V alloys, namely dilute bismide alloys and the promise they offer in terms of band structure engineering for highly efficient and thermally stable optoelectronic properties.

5. Dilute bismide alloys for highly efficient, temperature stable photonic components

We have described that telecom lasers based both on dilute nitride and on conventional III–V alloys suffer from significant intrinsic losses, particularly above room temperature. The observed degradation in device performance with increasing temperature is primarily due to the presence of Auger recombination and of IVBA processes [4]. By investigation of antimony-containing alloys such as InGaAsSb/GaSb it has been demonstrated that antimonide-based laser devices offer benefits such as reduced threshold current and temperature sensitivity in the 2–3 \( \mu m \) wavelength range [23]. These improved device characteristics have been attributed to the spin-orbit-splitting, \( \Delta_{SO} \), exceeding the band gap, \( E_g \). This leads to a suppression of the dominant CHSH Auger recombination mechanism due to the inability of such transitions to conserve energy for \( E_g < \Delta_{SO} \) (cf figure 7), and should also eliminate IVBA [23, 79]. Similar benefits have also been observed in GaInAsSbP mid-infrared light emitting diodes [80].

Achieving similar characteristics at telecom wavelengths has remained an elusive task—it has not been possible to effectively suppress Auger recombination at high temperatures. Sweeney et al recently proposed that by engineering the band structure to achieve \( \Delta_{SO} > E_g \), it should be possible to realise laser devices operating at telecommunication wavelengths with suppressed Auger...
recombination and IVBA and hence improved efficiency and temperature stability [23, 25].

Such a band structure could be achieved using alloys containing dilute amounts of bismuth (Bi), the largest stable group V element. Bismuth has a very large spin-orbit splitting of ≈ 2.2 eV and it has been demonstrated that incorporating dilute quantities of Bi in GaAs to form GaBi$_x$As$_{1-x}$ can give some highly interesting and unusual electronic properties.

Experimental investigations of GaBi$_x$As$_{1-x}$ alloys have revealed (i) a large downward bowing of the band gap, which reduces by ≈ 90 meV per percent Bi for x ≲ 5% [23, 24, 81, 82] and (ii) a large upward bowing of the spin-orbit-splitting. It has been demonstrated that these effects lead to the onset of a $\Delta_{SO} > E_g$ regime in the alloy for x ≈ 10% [23, 24]. Based on a comparison with the antimonides this latter characteristic is of great technological interest, opening up an avenue to suppress CHSH Auger recombination processes at sufficiently high Bi compositions. This could enable highly efficient photonic devices operating with reduced threshold current and temperature sensitivity at telecommunication wavelengths.

Bismuth, being the largest stable group V element, is significantly larger and more electropositive than As. It should therefore be expected Bi could give rise to impurity levels, as was the case for N. However, any Bi-related impurity states in GaAs should lie near or above the VB edge and, if an anti-crossing interaction occurs, it will occur between the Bi-related impurity levels and the VB edge of the host (GaAs) matrix. It has been proposed that the band structure of GaBi$_x$As$_{1-x}$ can be explained in terms of a VB BAC interaction [24, 82–84]. The presence of Bi-related states has been confirmed by several theoretical studies [24, 85], but there remains controversy as to whether or not the observed bowing of the band gap and spin-orbit-splitting with increasing Bi composition can be attributed to a BAC interaction occurring in the VB in GaBi$_x$As$_{1-x}$ [86]. Strong evidence for the BAC model in GaNAs is provided by the observation in photoreflectance of the $E_g$ transitions shown in figure 1(a). No equivalent transitions have been found in GaBiAs.

We presented in [24] a detailed investigation of the electronic structure of GaBi$_x$As$_{1-x}$ based on an $sp^3s^*$ tight-binding model. The model reproduces the measured variation of $E_g$ and $\Delta_{SO}$ with Bi composition in GaBi$_x$As$_{1-x}$ across the experimentally investigated composition range, to a high degree of accuracy and the observed crossover to a $\Delta_{SO} > E_g$ regime in the alloy for x ≈ 10%.

Based on this tight-binding model we have been able to gain several key insights into the electronic structure of GaBi$_x$As$_{1-x}$ and related alloys. Firstly, by considering GaP:Bi and explicitly demonstrating the validity of the BAC model as applied to the dilute bismide case, we showed that a BAC description of the GaBi$_x$As$_{1-x}$ VB edge is justified [84]. Secondly, we demonstrated that the absence of Bi-related features in spectroscopic measurements of GaBi$_x$As$_{1-x}$ is attributable to a strong broadening of the Bi-related states by the large density of GaAs valence states with which they are resonant (see figure 9 in [24]). Thirdly, detailed calculations on large ordered and disordered supercells showed that the large bowing of $E_g$ with Bi composition arises not only from a strong upward shift of the alloy VB edge with composition (due to anticrossing with lower lying Bi-related states), but that a significant conventional alloy reduction in the CB edge energy also contributes to the observed reduction in the band gap. Finally, the spin-split-off band edge was found to admit a description in terms of a conventional alloy model, similar to the CB edge, but varying less strongly in energy with Bi composition. The observed strong bowing of $\Delta_{SO}$ is then attributed primarily to the BAC-induced upward shift of the VB edge [24, 84]. Figure 9(a) shows the predicted variation in the band edge energies calculated using the tight-binding model. The resulting variation in the band gap and spin-orbit-splitting calculated for a series of large, disordered, free-standing GaBi$_x$As$_{1-x}$ supercells is compared with experimental data in figure 9(b).

Based on the tight-binding results, we have extended the 8-band $k \cdot p$ model to include four Bi-related resonant states in a 12-band $k \cdot p$ model for (In)GaBi$_x$As$_{1-x}$. Calculations based on this $k \cdot p$ model [84] provide results in excellent agreement with PR measurements [23, 87] of $E_g$ and $\Delta_{SO}$ for a series of molecular beam epitaxy (MBE)-grown epitaxial GaBi$_x$As$_{1-x}$/GaAs layers. This modified $k \cdot p$ model is currently being applied to further investigate the electronic and optical properties of dilute bismide alloys and the potential of optimised bismide-based photonic components operating at telecommunication wavelengths.

The tight-binding analysis has also been extended to the quaternary dilute bismide-nitride alloy GaBi$_x$N$_y$As$_{1-x-y}$ [88]. Co-alloying N and Bi in GaAs offers further potential for band structure engineering to design highly efficient and temperature insensitive photonic components operating at telecom and longer wavelengths. The large variation in the GaN$_x$As$_{1-x}$ and GaBi$_x$As$_{1-x}$ band gaps with nitrogen and bismuth composition enables the GaBi$_x$N$_y$As$_{1-x-y}$ material system to span a wide wavelength range, even when grown on a GaAs substrate. Since N and Bi in GaAs introduce, respectively, tensile and compressive strain, the N and Bi compositions in GaBi$_x$N$_y$As$_{1-x-y}$ can be chosen to lattice-match the alloy to a GaAs substrate, while allowing access to the 1.3 $\mu$m and 1.5 $\mu$m wavelength ranges and beyond. Theoretical calculations have shown that GaBi$_x$N$_y$As$_{1-x-y}$ retains the large upward bowing of the spin-orbit-splitting present in GaBi$_x$As$_{1-x}$ [88]. Because co-alloying Bi with N causes a giant reduction in the band gap, this offers the possibility to eliminate the CHSH Auger recombination mechanism in lasers operating across a wide wavelength range, from 1.5 $\mu$m through to mid-infrared wavelengths [89].

By examining in detail the effects of co-alloying N and Bi in a series of ordered GaBi$_x$N$_y$As$_{1-x-y}$ supercells using the tight-binding model, we showed that the effects of Bi and N on the GaAs electronic structure are largely decoupled from each other [84, 88, 90]. This indicates that the GaBi$_x$N$_y$As$_{1-x-y}$ electronic structure admits analysis in terms of separate N- and Bi-induced BAC interactions occurring in the CB and VB, respectively [84]. Based on this, we have derived a 14-band $k \cdot p$ model of GaBi$_x$N$_y$As$_{1-x-y}$, which is in good agreement with tight-binding calculations on both ordered [84] and disordered...
Figure 9. (a) Calculated variation of the band edge energies of the lowest CB, top two VBs and spin-split-off band, with Bi composition in GaBi$_{1-x}$As$_1$−$_x$, using an sp$^3$s$^*$ tight-binding model. (b) Solid lines/Closed black points: Calculated variation the band gap ($E_g$) and spin-orbit-splitting ($\Delta SO$), as a function of Bi composition in GaBi$_{1-x}$As$_1$−$_x$, using an sp$^3$s$^*$ tight-binding model. Various symbols: Experimental measurements of $E_g$ and $\Delta SO$ from the indicated sources. ((a) and (b) reprinted with permission from [24]. Copyright of the American Physical Society (2011).)

GaBi$_x$N$_y$As$_{1-x-y}$ supercells. Figure 10(a) shows the variation of the band gap as a function of Bi and N composition for GaBi$_x$N$_y$As$_{1-x-y}$ epitaxially grown on GaAs, calculated using the 14-band $k\cdot p$ model of [84]. This shows the wide wavelength range accessible using GaBi$_x$N$_y$As$_{1-x-y}$ grown on a GaAs substrate. Figure 10(b) shows the calculated difference between the spin-orbit-splitting and the band gap energy over the same composition range, showing the regions in which $\Delta SO > E_g$ and suppression of CHSH Auger recombination can be expected.

In addition to GaBi$_x$N$_y$As$_{1-x-y}$/GaAs, the In$_{1-x}$Ga$_x$Bi$_y$As$_{1-y}$/InP system offers similar promise for mid-infrared applications. Figure 11 shows the calculated and measured variation of $E_g$ and $\Delta SO$ as a function of In and Bi composition for material lattice-matched to InP [91]. Here it is seen that the spin-orbit-splitting exceeds the band gap for $\sim$3–4% bismuth. This illustrates the potential of this system to cover a wavelength range in the near-infrared, while being close to lattice matched with InP.

The prospect of achieving $\Delta SO > E_g$ at telecom wavelengths has sparked increasing interest in the growth, characterization, and understanding of dilute bismide alloys. High quality growth of GaBi$_x$As$_{1-x}$ on a GaAs substrate has been reported using MBE by Lu et al [92], showing Bi incorporation of up to $\sim$10%. This is just sufficient to shift the band gap energy into the 1.5 $\mu$m range with $\Delta SO > E_g$, as confirmed by the photo-modulated reflectance (PR) measurements of Batool et al [87] included in figure 9. Room temperature photoluminescence (PL) was obtained from these samples across the full range of compositions, with the maximum PL efficiency in samples with $x \sim 4.5\%$ consistent with reports from other growth groups. By reducing the growth temperature, further MBE samples have been grown with $x$ as high as 20% [93]. In other work, Mazur et al [94] have reported the growth of an 11 nm GaBi$_x$As$_{1-x}$/GaAs ($x \sim 6\%$) QW structure with low dislocation density confirmed by high-resolution x-ray diffraction (HR-XRD), exhibiting low temperature PL with a linewidth of $\sim$40 meV. More recently, Ludewig et al [95] have reported the droplet-free epitaxial growth of GaBi$_x$As$_{1-x}$ multiple QW structures on a GaAs (001) substrate by metal organic vapour phase epitaxy using all-liquid group V precursors under controlled growth conditions. HR-XRD, transmission electron microscopy and atomic force microscopy measurements showed that the MQW structures grown had good crystalline quality, with bismuth concentrations of up to 4.2%. Room temperature PL was observed, where the peak position shifted to lower energies and the integrated PL signal decreased with increasing Bi fraction. Zhong et al [96] have demonstrated the growth of In$_x$Ga$_{1-x}$Bi$_y$As$_{1-y}$ layers on InP where the bismide layers contained up to 6.75% Bi. In terms of progression towards devices, GaAsBi/GaAs light emitting diode structures have been fabricated with low ($<2\%$) Bi fraction exhibiting electroluminescence (EL) at room temperature [97]. However, the device performance was limited by defect-related recombination and carrier leakage due to the small CB offset. Optically pumped lasing has been demonstrated from a bulk-like GaBi$_{0.025}$As$_{0.975}$ layer sandwiched between GaAs confinement layers [98]. Overall, the growth and characterization of high quality bismide samples, primarily on GaAs substrates has seen rapid progress over the last few years.
Figure 10. Calculated room temperature variation of (a) the band gap and (b) the difference between the band gap and spin-orbit-splitting ($E_g - \Delta_{SO}$), as a function of Bi and N composition, $x$ and $y$, for GaBi$_x$N$_y$As$_{1-x-y}$ epitaxially grown on GaAs. The solid lines in (a) denote paths in the composition space along which the band gap is constant; dashed lines denote paths along which the strain is constant. The solid lines in (b) denote paths in the composition space along which $E_g - \Delta_{SO}$ is constant; dashed lines denote paths along which the strain is constant. Regions in (b) where $\Delta_{SO} > E_g$ (to the right of the $E_g = \Delta_{SO}$ contour) indicate alloys in which suppression of CHSH Auger recombination and IVBA can be expected to occur.

Figure 11. Measured variation in the band gap and spin-orbit splitting energies of InGaAsBi alloys grown on InP using multiple spectroscopic techniques. Also shown are the calculated variations of the band gap and spin-orbit splitting as a function of Bi and In fraction [91].

6. Discussion and conclusions

In summary, we have reviewed that highly mismatched semiconductor alloys such as GaN$_x$As$_{1-x}$ and GaBi$_x$As$_{1-x}$ have several novel electronic properties, including a rapid reduction in energy gap with increasing $x$. This has opened the possibility to achieve longer wavelength emission on GaAs. Theoretical calculations have shown that the gain and loss characteristics of ideal dilute nitride lasers should be at least as good as those of conventional InP-based telecom lasers. Substantial progress was made in the development of GaInNAs telecomm lasers, leading to the demonstration of 1.3 $\mu$m edge-emitting and vertical cavity lasers [12] as well as devices emitting at 1.5 $\mu$m and beyond, with characteristics comparable to conventional InP-based devices. Overall good characteristics have been demonstrated by dilute nitride lasers, but the advantages of using dilute nitrides e.g. in VCSEL structures have not been sufficiently pronounced to displace the well-tested incumbent technology based on InP. We note that the lack of uptake of dilute nitride based lasers was at least in-part driven by economic uncertainty in the telecomms industry during the mid-2000s where some of the most successful commercial producers of devices left the sector. This led to a large loss of momentum in the development of the technology. However, dilute nitrides are making a resurgence, for example, as the 1 eV junction in multi-junction solar cells which currently hold the efficiency record of 43.5% [100, 101] and for use in III–V alloys for direct integration of lasers with silicon [102], both of which are proving to be promising applications of this interesting class of materials.

The measured threshold current in dilute nitride devices includes a large Auger contribution to the total current, similar to that found in conventional InP-based devices. Combined with the persistence of IVBA in dilute nitride lasers, this can lead to a strong temperature dependence of the threshold current and optical emission characteristics, as is also the case
for InP-based devices. Considerable benefit would be obtained by eliminating these loss mechanisms from telecom devices. We have shown that a very large spin-orbit-splitting energy, $\Delta SO$, can be achieved in GaBiAs alloys, with $\Delta SO$ exceeding the energy gap $E_g$ for Bi compositions above 10% and emission wavelengths around 1.5 $\mu$m. The growth of GaBiNAs or of GaInBiAs on InP can extend this condition to longer wavelengths. We have described that achieving $\Delta SO > E_g$ should suppress IVBA and the dominant Auger recombination loss mechanism both in telecom and in mid-infrared lasers. We argue that the introduction of dilute bismide alloys should therefore finally allow a route to achieve efficient temperature-stable lasers with significantly reduced power consumption at telecom and longer wavelengths, offering considerable benefits for a wide range of applications.

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