The temperature dependence of the fundamental band gap energy of semiconductors represents a basic material-specific property which is of considerable practical and also theoretical interest. It is known from many experimental results that the band gap of a semiconductor decreases monotonically with increasing temperature. The two main contributions to this are shifts of the band edges due to: (i) dilation of the lattice constant with increasing temperature; and (ii) the temperature dependent electron–phonon interaction [1]. There are several commonly employed models or parameterizations of the temperature dependence of the band gap of semiconductors. These include the Bose–Einstein [2, 3] and O’Donnell models [4]. However, the most frequently used formula for approximate parameterization of band gap energy as a function of temperature is the one proposed by Varshni,

$$E_g(T) = E_g(0) - AT^2/(B + T)$$

where $A$ and $B$ are constants [1].

The temperature dependence of the band gap of conventional III–V semiconductors such as GaAs, GaSb or InP can be modified by the substitution of nitrogen onto the group V sub-lattice. It has been shown that the incorporation of a few

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**Nitrogen pair-induced temperature insensitivity of the band gap of GaNSb alloys**

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**Abstract**

The temperature dependence of the band gap of GaN$_x$Sb$_{1-x}$ films with $x \leq 1.3\%$ has been studied in the 1.1–3.3 μm (0.35–1.1 eV) range using infrared absorption spectroscopy between 4.2 and 300 K. As with other dilute nitride semiconductors, the temperature dependence of the band gap is reduced by alloying with nitrogen when compared to the host binary compound. However, for GaNSb, the smallest variation of the band gap with temperature is observed for samples with the lowest N content for which the band gap is almost totally insensitive to temperature changes. This contrasts with the more widely studied GaN$_x$As$_{1-x}$ alloys in which the band gap variation with temperature decreases with increasing N content. The temperature-dependent absorption spectra are simulated within the so-called band anticrossing model of the interaction between the extended conduction band states of the GaSb and the localized states associated with the N atoms. The N next-nearest neighbor pair states are found to be responsible for the temperature insensitivity of the band gap of the GaNSb alloys as a result of their proximity to the conduction band edge giving them a more pronounced role than in GaNAs alloys.

**Keywords**: GaSb, dilute nitride, band gap, band anticrossing, GaNSb

(Some figures may appear in colour only in the online journal)
percentage of nitrogen in Ga(In)As reduces the temperature-induced shift of the band gap energy by 12% in GaInNAs [5] and 40% in GaNAs [6] compared to GaAs. The effect has been ascribed to the interaction of temperature-insensitive localized N states with extended band states that have a temperature dependence close to that of GaAs [6, 7]. For GaNAs, the temperature dependence of the band gap decreases as the N content is increased, suggesting the possibility of increased temperature insensitivity of the band gap, a desirable material property for device applications.

Introducing a small amount of nitrogen into the host III–V semiconductor causes a strong reduction of the band gap energy. This reduction has been already observed in the dilute nitrides GaNAs [6], GaInNAs [5], GaNP [9], GaNSb [8] and also in InNAs [10] and explained by a two level conduction band anticrossing model (BAC) where the interaction between the host conduction band and resonant nitrogen level results in the formation of two nonparabolic subbands [11, 12]. Recent studies of GaNSb have shown that a three level BAC model, where additional N nearest-neighbor pair states play a significant role [13, 14], much better reproduces the evolution with N content of the lowest absorption edge [15]. Additionally the linear combination of isolated nitrogen states (LCINS) model proposed by O’Reilly et al has also given good results [16, 17].

Unlike in most other cases, where a reduction in band gap energy is achieved by inserting an element that increases the lattice constant, nitrogen accomplishes this and at the same time reduces the lattice constant. These phenomena have important implications for developing new materials systems. For example, by substituting specific ratios of nitrogen and indium into GaAs, forming GaInNAs, the lattice parameter can be matched to that of GaAs while simultaneously reducing the band gap [18]. This approach also offers the prospect of lattice matched GaInNSb and GaNSbBi alloys with tunable band gaps for mid-infrared optoelectronic devices, including sources and detectors for the 2–5 micron atmospheric transmission window, thermophotovoltaics and lasers [15, 19]. For these applications, a temperature independent band gap is a desirable property, but there are no previous reports of the GaNSb band gap as a function of temperature.

Here, unexpected temperature insensitivity of the band gap of GaNSb alloys is demonstrated with least temperature dependence for the lowest N content. (The models employed here based on perturbation theory approaches do not have a threshold at which the BAC behaviour switches off, but there will be some threshold below which the models no longer apply. Here we have not explored samples with an N content below 0.18% of the anion sublattice. However, previous tight binding results for GaNSb depict the band anticrossing phenomenon for 3 N atoms out of 864 anion lattice sites, a N content of 0.35% ([20]) and magneto tunnelling spectroscopy has previously given evidence of the band anticrossing E versus k dispersion for GaNAs with as little as 0.08% N ([21]). First principles calculations of GaNAs and GaNSb are consistent with these experimental and tight binding results [22]). This temperature insensitivity is found to be due to the presence of a localized state associated with N pairs below the conduction band edge of the host GaSb material. This behavior is explained within the three level BAC model. Such a strong degree of temperature insensitivity has not been observed before in more widely studied Ga(In)NAs alloys, where the N pair states in this material do not play such a significant role and the simple two level BAC model is sufficient to describe the changes of the band gap as a function of temperature [6].

The samples used in this work are 2 μm thick GaN x Sb1−x films grown by plasma assisted molecular beam epitaxy (MBE) on semi-insulating GaAs(011) substrates at QinetiQ Ltd., Malvern. The N contents determined from high-resolution x-ray diffraction reciprocal space mapping measured on a Panalytical XPert Pro MRD equipped with a 4-bounce Ge 220 Hybrid monochromator giving pure Cu Kα1 radiation and a triple-axis monochromator. The N content was varied by changing the substrate temperature with a fixed growth rate of 0.8 μm h⁻¹ ([23]). A GaSb reference film of 2 μm thickness was grown by MBE on semi-insulating GaAs(001) at the University of Warwick. Reflectance and transmittance measurements were performed in the temperature range from 4 to 300 K using a Bruker Vertex 70V Fourier-transform infrared spectrometer (FTIR), using a liquid nitrogen-cooled HgCdTe detector with a working range between 0.05 and 1.2 eV and using a continuous flow helium cryostat (Oxford Optistat CF-V). The absorption coefficient, α, was calculated from the transmission and reflectance data using equation (1) in [15]. A gold mirror was used as the reflection standard. The angle of incidence for reflection and transmission measurements was 11° with respect to the surface normal of the sample. The FTIR spectra were recorded with the resolution set to 1 meV. Hall effect measurements using the Van der Pauw configuration were used to determine the carrier concentration and mobility at room temperature (295 K) and liquid nitrogen temperature (77 K).

The reciprocal space maps (RSMs) for the 224 and 004 reflections for one of the samples are shown in figure 1 in reciprocal lattice units. X-ray diffraction RSMs of the GaN x Sb1−x samples grown on GaAs substrates were used to determine the alloy composition. As the GaN x Sb1−x epilayers are ∼2 μm thick they are expected to be close to 100% relaxed. In order to be able to account for any tetragonal distortion, two dimensional reciprocal space mapping of the 224 and 004 Bragg peaks has been performed to enable the composition and degree of relaxation to be determined. The data in figure 1 is from a film determined to have a N content of 1.3% and relaxation of 95.5%. This degree of relaxation can be seen in the 224 RSM where the GaSb epilayer peak is close to the line corresponding to full relaxation. The N content of the films was found from the RSMs to be in the range of 0.18%–1.3% of the group V sublattice with 95%–98% relaxation.

Hall effect results are shown in figure 2 for 77 and 295 K. All the films are p-type with hole density (mobility) in the range (1.6–5.5) × 10¹⁸ cm⁻³ (180–104 cm² V⁻¹ s⁻¹) for all the GaN x Sb1−x films and 2 × 10¹⁶ cm⁻³ (730 cm² V⁻¹ s⁻¹) for the GaSb film. The absorption spectra obtained at different temperatures for the p-type GaSb layer grown on a GaAs substrate are
The exciton peak appears up to 90 K. The band gap behavior as a function of temperature is shown in figure 4(a); values from 100 to 300 K were found using standard linear extrapolation to the background intensity of $\alpha$ versus $h\nu$ curves, while values from 4.2 up to 90 K were obtained using the exciton peak position plus the Rydberg energy of 1.4 meV [25]. The oscillations below the absorption onset for each temperature are due to the Fabry–Perot interference associated with the GaSb film thickness. The band gap decreases by 92 meV between 4 and 300 K.

Absorption spectra for different temperatures of two GaN$_x$Sb$_{1-x}$ films are shown in figures 3(b) and (c). In each sample, the absorption coefficient generally increases with increasing temperature, which is typical for direct band-gap semiconductors. With increasing temperature the absorption edges shift to lower energies, while the line shape (base line and slope) remains essentially unchanged. However, the shift of the lowest absorption edge with temperature is much smaller than the shift of absorption edge of the host GaSb and becomes greater for the samples with higher N content; the absorption edge shifts to lower energy between 4 and 300 K are 40, 74 and 84 meV for 0.18%, 0.34% and 1.3% N, respectively. This behavior is opposite to the case of GaNAs, where the absorption edge shift is reduced with increasing N content [6, 7].

The effect observed here for GaN$_x$Sb can be described by the three level BAC model. The band structure of GaN$_x$Sb$_{1-x}$ with $x = 0.013$ is shown in figure 3(d) and has been calculated using a three level BAC model with impurity levels associated with isolated N atoms and N second-nearest-neighbor pairs, where a Ga atom has two N neighbors, interacting with the host conduction band, resulting in the formation of three non-parabolic subbands [14, 15, 17], described by the Hamiltonian

$$H = \begin{bmatrix}
E_C(k) & V_{MN} & V_{MMN} \\
V_{MN} & E_N & 0 \\
V_{MMN} & 0 & E_{NN}
\end{bmatrix},$$

(1)

where $E_N$ and $E_{NN}$ are the isolated N and N pair impurity level energies, and $V_{MN} = \beta_{MN}^{1/2}$ and $V_{MMN} = \beta_{MN}^{1/2}$ denote the BAC coupling matrix elements. Here the statistically expected concentration of N pairs, $x_{NN}$, is $6x^2$, where $x$ is the total N content, and the concentration of isolated N atoms, $x_N$, is taken as $x = 2x_{NN}$. Additionally, it should be noted that the host GaSb conduction band, $E_M(k)$, includes the Kane nonparabolicity, due to interactions with the light-hole, heavy-hole and split-off bands, described by the $(4 \times 4) k \cdot p$ Hamiltonian introduced by Pidgeon and Brown in [26]. The anticrossing between the host conduction band, N level and N pair level is clear, creating three subbands ($E_1$, $E_2$ and $E_3$—see figure 3(d)). The lower of these two subbands, of largely conduction band $s$-like character close to $\Gamma$, is below the conduction band minimum of the host semiconductor (GaSb), causing a reduction of the fundamental band gap. With increasing N content, the anticrossing interaction becomes stronger, leading to a reduction in energy of the $E_1$ and $E_2$ bands and an increase in the energy...
of the $E_3$ band, increasing their separation and reducing the fundamental band gap.

The BAC parameters used in the modelling were optimized to reproduce the experimentally determined evolution with temperature and N content of the band edge positions from the absorption onsets. Previously we reported, from three level BAC modelling of room temperature absorption data, the impurity levels to be $E_N = 0.82$ eV and $E_{NN} = 0.48$ eV above the valence band maximum [15]. Here, the measurements were performed over a wide temperature range and the modelling additionally includes band gap renormalization and broadening, enabling the impurity level values to be determined more accurately, giving values of $E_N = 0.85$ eV and $E_{NN} = 0.55$ eV above the valence band maximum. By fitting to the absorption onsets values, the optimum values of $\beta_N$ and $\beta_{NN}$ were found to be 2.3 eV and 3.25 eV, respectively, similar to those reported in [15].

Calculated absorption curves are shown in figures 3(e) and (f). The calculated absorption spectra were simulated using the method described by Perlin et al [27], extended to include N pair states as reported in [15, 17]. It is based on the calculation of the joint density of states for each electronic transition. It also includes band gap renormalization whereby interactions between the free carriers and with the ionized impurities lead to a narrowing of the band gap in semiconductors [28]. The calculated band gap renormalization for all the GaNSb samples is in the range 40–50 meV. Additionally, to account for extrinsic broadening and temperature dependent broadening of experimental spectra due to electron–phonon interactions, a Gaussian function was convoluted with the simulated energy-dependent absorption coefficient. The broadening parameter, $\Gamma(T)$, of the Gaussian varied with temperature according to the formula, $\Gamma(T) = \Gamma(0) + \Gamma_{LO}[\exp(\theta_{LO}/T) - 1]$, where $\Gamma_{LO}$ is the electron-longitudinal optical (LO) phonon coupling constant, and $\theta_{LO}$ is the LO phonon temperature. The parameter $\Gamma(0)$ accounts for intrinsic broadening and extrinsic broadening mechanisms such as impurity and alloy scattering [29].

The absorption edges as a function of temperature of GaSb and Ga$_x$Sb$_{1-x}$ with different N compositions of 0.18%, 0.34% and 1.3% are presented as open circles with error bars in figure 4. The temperature dependence of the band gap energy of the GaSb was parameterized using the conventional Varshni relation, $E_g(T) = E_g(0) - AT^2/(B + T)$. $E_g(0)$ is the band gap at $T = 0$ K while $A$ and $B$ are the Varshni coefficients. The parameters fitted for GaSb were found to be $E_g(0) = 0.811$ eV, $A = 4.97 \times 10^{-4}$ eV K$^{-1}$, and $B = 185$ K which are very close to Vurgaftman et al’s recommended values [30]. These values were used to describe the temperature dependence of the host GaSb band gap in the modelling of the temperature dependent GaNSb absorption spectra. Very similar fits to the temperature dependence of the band gap of GaSb were also obtained using the Bose–Einstein formula [2].

The calculated variation of the band gap with temperature is shown for the GaNSb samples by the solid lines in figure 4. This shows that the three level BAC model predicts only 1.3, 2.5 and 29 meV reduction in band gap between 4 and 300 K for GaNSb with N contents of 0.18%, 0.34% and 1.3%, respectively. This reduction of the band gap in this temperature range is significantly less than the corresponding measured reduction of the absorption edges of 40, 74 and 84 meV. The addition of temperature dependent broadening to the calculated absorption spectra is required to reproduce the experimental temperature dependence of the absorption edges; the calculated variation of the absorption edge with temperature including this broadening for the different samples is depicted by the dot-dashed lines in figure 4. Once broadened, the absorption edge onset energy of each calculated absorption spectrum is taken to be the result of fitting the linear portion of $\alpha^2$ versus $h\nu$ and extrapolating to zero absorption coefficient. The maximum broadening, $\Gamma$, which
occurs at the highest temperature of 300 K, is in the range 50–70 meV for all the GaNSb samples. This is in the range of the broadening previously reported for GaAs, GaP and GaN [31].

Figure 5 shows the temperature dependence of the energy shift of the band gap of GaN\textsubscript{1−x}Sb\textsubscript{x} alloys calculated using two different models: the two level BAC model, neglecting the N pair level (in figure 5(a)) and the three level BAC model including the N pair level (in figure 5(b)). In contrast to GaN\textsubscript{1−x}As\textsubscript{x} alloys [7], a small temperature dependence of the band gap is observed for the very lowest N content of 0.18%–40 meV between 4 and 300 K, corresponding to a band gap reduction of about 1 meV and a ~39 meV downward shift of the absorption edge due to electron–phonon interaction-induced broadening. This difference from GaNAs is because for that material, the N pair level does not play a significant role and so the two level BAC model is sufficient to describe the absorption edge evolution as a function of temperature [20]. In the case of GaN\textsubscript{1−x}Sb\textsubscript{x}, the N pair level has a much greater influence on the evolution of the absorption edge as a function of both N content and temperature.

For the lowest N content of 0.18%, the density of states is very small for the lowest conduction subband, therefore the absorption edge is determined by a combination of E\textsubscript{1} and E\textsubscript{2} subbands. The middle E\textsubscript{2} subband is repelled by the lowest E\textsubscript{1} subband preventing it from moving below the N pair level,
even though increased temperature drives it downwards in energy. For the largest N content of 1.3%, the density of states for the lowest conduction subband \( E_1 \) is much larger; therefore it fully determines the lowest energy absorption edge. In this case, the subband which determines the lowest absorption edge is not trapped by repulsion by a nearby level so the temperature dependence is larger.

In figure 6, the calculated evolution of the subband energies with N content is plotted for a temperature of 50 K along with the experimental absorption onsets. This shows that the 3-level BAC model provides a better description than the 2-level BAC model for all three N contents measured here. But it is expected that for some composition below 0.18% N, the 2-level BAC model will provide the best description of absorption data.

In order to consider the effects of lifetime broadening, the densities of states for different temperatures, calculated using Green’s function implementation of the many impurity Anderson model \[32\] for two GaNSb compositions are presented in figure 7 and the insets contain the density of states calculated using the two level BAC model. These calculations confirm the findings detailed above from comparison of the experimental absorption spectra with those calculated using the three level BAC model. That is, the presence and energy position of the N pair level strongly influences the band gap evolution with N content and also its temperature dependence.

The change of temperature dependence of the band gap as a function of N content can be illustrated by the evolution of the derived Varshni \( A \) parameter as a function of composition. The determined Varshni parameter \( A \) as a function of composition, using two level and three level BAC models is presented in figure 5(c). The parameter \( B \) was kept constant and equal to the value for the host GaSb. In the two level BAC model, the parameter \( A \) monotonically decreases with increasing N content and asymptotically tends to \( 2.5 \times 10^{-4} \) eV K\(^{-1}\)—this corresponds to greater absorption edge shift for low N content and smaller absorption edge shift for higher N contents. This is the phenomenon previously observed for GaNAs \[7\].

Additionally, the slope of the curve is negative and changes from being very steep for low N content to shallow for higher N contents, indicating that the amount of absorption edge shift with temperature plateaus with increasing N content.

For the case of three level BAC, the situation is different. Here, the parameter \( A \) monotonically increases with increasing N content from \( A \sim 0 \) eV K\(^{-1}\) and this corresponds to greater absorption edge shift with increasing N content. The slope of the curve is always positive, but it changes from being initially shallow (up to 0.25% N) to being steep (between 0.25% and 1.5% N) and then plateaus with increasing nitrogen concentration. Hence, the rate of change of absorption edge shift is small for very low N concentration, increases and finally reduces again with increasing N content. These phenomena are illustrated by the arrows in figures 5(a) and (b).

In conclusion, the temperature dependence of the optical gap of GaN\(_x\)Sb\(_{1-x}\) films has been studied by FTIR absorption spectroscopy and understood in terms of a three level band anticrossing model in the range of 4–300 K. The experimental data have been well reproduced using the three level BAC model modified including the effects of band gap renormalization and Gaussian broadening. By the comparison of experimental to modeled spectra, the position of isolated N and N pair levels have been determined to be \( E_N = 0.85 \) eV and \( E_{NN} = 0.55 \) eV. A decrease in the energy of the absorption onset has been observed with increasing temperature.
However, an unexpected trend was found of energy gap change with temperature as a function of N content—the temperature insensitivity of the band gap is greatest for GaN$_x$ Sb$_{1-x}$ samples with low N content in contrast to dilute GaN$_x$ As$_{1-x}$ alloys.

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