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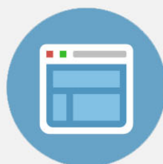

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Optical absorption by dilute GaNSb alloys: Influence of N pair states

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The optical properties of GaNSb alloys with N contents of up to 2.5% have been investigated at room temperature using infrared absorption spectroscopy. The evolution of the absorption onsets with N content has been described using a three level band anticrossing model of the N localized states interactions with the GaSb conduction band. This approach includes the effect of N pair states, which is critical to reproduce the observed optical properties. This confirms theoretical predictions that N pair states have a more pronounced effect on the band dispersion in GaNSb than in GaNAs. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4816519]

GaSb-based compounds are attractive for mid-infrared optoelectronic devices, including sources and detectors for the 2–5 micron atmospheric transmission window, lasers, and improved efficiency thermophotovoltaics. One so far under exploited method of tuning the band gap of GaSb-based compounds is to substitute up to a few percent of the Sb atoms with N atoms. This simultaneously reduces the band gap and the lattice constant in contrast to conventional alloying, such as with indium, wherein reducing the band gap increases the lattice constant. This offers the prospect of lattice matched GaInNSb alloys[1] with tunable band gaps, just as with the more widely studied GaInNAs system.

Band gap reduction[2–4] and the band anticrossing (BAC) phenomenon[3,5] have both previously been observed for GaNSb alloys with up to 1.5% N. Indeed, excellent agreement was obtained as a function of N content between the highest energy absorption onsets observed and modeling of the transitions from the light and heavy hole valence bands to the so-called E_+ conduction subband.[3] However, no such quantitative agreement was obtained for the absorption onsets said to be associated with transitions from the highest valence bands to the E_- conduction subband. It was suggested, but not proven, that the failure to model the evolution of the E_--related absorption onsets may have been associated with valence band tail states due to the relatively high free hole densities in the films of $(3–6)\times10^{18}\,\mathrm{cm}^{-3}$.[3]

In this Letter, Fourier transform infrared (FTIR) absorption measurements of GaNSb films are presented and analyzed within the band anticrossing model. By additionally incorporating the effects of N pair states within the many impurity Anderson model approach, it is shown that the band gap reduction is greater than previously suggested and the low energy absorption edges observed are not related to defect-induced valence band tails.

Two sets of $\mathrm{GaN}_x\mathrm{Sb}_{1-x}$ samples were grown by plasma assisted molecular-beam epitaxy (MBE). The first set was grown to a thickness of approximately 2 μm (1.5 μm for the GaSb film) on semi-insulating GaAs(001) substrates at QinetiQ Ltd., Malvern with N contents determined from x-ray diffraction reciprocal space mapping to vary from 0.18 to 1.63%. In this case, the N content was varied by changing the substrate temperature during growth with a fixed growth rate of 0.8 $\mu\mathrm{m\,h}^{-1}$.[6] The second set was grown to a thickness of 0.4 μm on GaSb(001) substrates at the University of Warwick with N contents determined from x-ray diffraction of 0.55 to 2.49%, varied by altering the growth rate at a fixed growth temperature of 320 °C.[1,7]

Reflectance and transmittance measurements were performed at room temperature using a Bruker Vertex 70 V Fourier-transform infrared spectrometer, using a liquid nitrogen-cooled mercury cadmium telluride detector with a working range between 0.05 and 1.2 eV. The absorption coefficient, α, was calculated using the equation[8]

$$T = \frac{(1-R^2)\exp\{-\alpha d\cos\theta\}}{1-R^2\exp\{-2\alpha d\cos\theta\}}, \quad (1)$$

where T is the transmission, R is the reflectance, α is the absorption coefficient, d is the epilayer thickness and θ is the angle of incidence with respect to the surface normal, 11° in this case. Hall effect measurements using the Van der Pauw configuration were conducted on the samples with GaAs substrates. These indicated that the GaSb film has a carrier density of $p = 2\times10^{16}\,\mathrm{cm}^{-3}$ and the GaNSb films all have a carrier density in the range $p = (3–6)\times10^{18}\,\mathrm{cm}^{-3}$.

Absorption spectra are shown in Fig. 1(a) for the $\mathrm{GaN}_x\mathrm{Sb}_{1-x}$ films grown on GaAs substrates. Calculated

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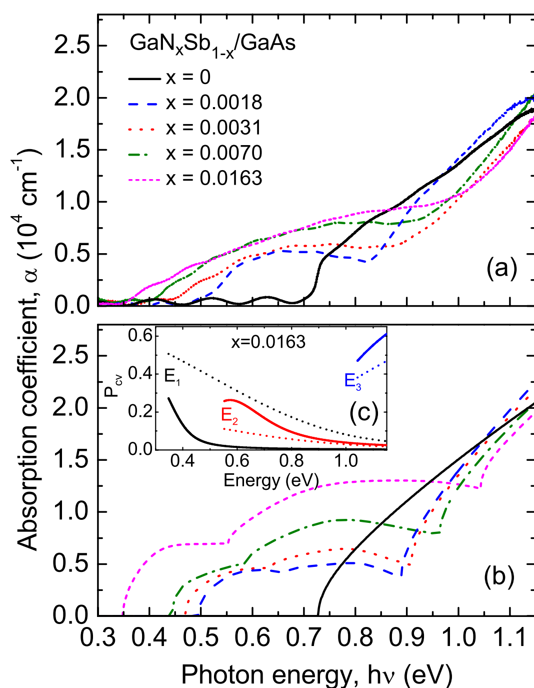

FIG. 1. (a) Absorption spectra from GaN$_x$Sb$_{1-x}$ with $0 \le x \le 0.0163$ grown on GaAs substrates. (b) The calculated absorption spectra, neglecting lifetime broadening, but including the momentum matrix elements shown as a function of energy in (c). In (c), the solid (dotted) lines represent the momentum matrix elements for transitions from the heavy (light) hole valence band to each of the conduction subbands, E_1, E_2, and E_3.

absorption curves are also shown in Fig. 1(b) and will be described later. For GaSb ($x = 0$), there is a single absorption onset at ~0.72 eV and below this energy are Fabry-Perot oscillations associated with the 1.5 μm GaSb film thickness. This onset corresponds to the room temperature band gap of GaSb.[8,9] Upon introduction of N into the GaSb, the absorption spectra exhibit two distinct onsets, one below and one above 0.72 eV, which diverge as the N content is increased.

The evolution of these onsets as a function of N content is shown by the closed circles in Fig. 2. The values for this plot were obtained by linear extrapolation to the background intensity of α^2 versus $h\nu$ curves. While strictly only valid for the purposes of obtaining band gap values when the conduction band is parabolic, this method was applied as the conduction band is parabolic very close to the Γ point, making it more appropriate than taking values from a plot of α versus $h\nu$ or $(\alpha h\nu)^2$ versus $h\nu$. Also shown is the evolution with N content of low energy absorption onsets for GaN$_x$Sb$_{1-x}$ films grown on GaSb substrates. For these samples, the higher energy absorption onsets are not seen because the GaSb substrate is not transparent at the corresponding wavelengths. All the measured data and trends are entirely consistent with previous studies for x values up to 0.015 in which modeling was either not employed or failed to reproduce the lowest energy absorption onset as a function of N content.[3,4] For both sets of data shown in Fig. 2, there is an initial steep decrease of the absorption edge on going from GaSb to the lowest N content GaN$_x$Sb$_{1-x}$ sample; for an x value of as low as 0.0018, the absorption edge decreases to 0.55 eV from 0.72 eV for GaSb. This corresponds to an initial decrease in band gap of about 0.9 eV/N%. Thereafter, there is a relatively shallow linear decrease of the absorption edge with

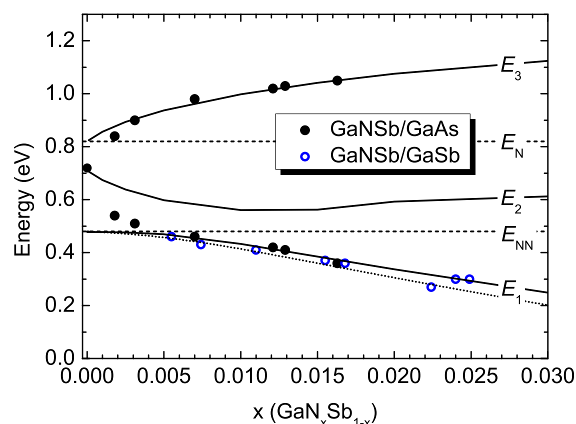

FIG. 2. The highest and lowest energy absorption onsets as a function of N content for GaNSb samples grown on GaAs (closed circles) and low energy absorption onsets as a function of N content for GaNSb samples grown on GaSb (open circles). The solid lines depict the evolution of the conduction subbands as a function of N content, as modeled using the many impurity Anderson model, including the isolated N states, N pairs states, and lifetime broadening. The dashed lines represent the energies of the isolated N level, E_N, and the N pair level, E_{NN}, used in the modeling. The dotted line shows the evolution of the lowest conduction subband as a function of N content, as modeled with the three level BAC model neglecting lifetime broadening. The zero of the energy scale corresponds to the valence band maximum.

increasing N content of 0.11 eV/N%, with the band gap reaching 0.30 eV for $x = 0.025$. Therefore, highly accurate compositions do not need to be achieved for an alloy with a particular band gap to be obtained. The compositional control already achieved is sufficient.[1,7]

Just as for the previous GaNSb absorption data of Jefferson *et al.*,[3] a simple two level band anticrossing model is able to reproduce the variation of the high energy onsets with N content, but not the lower energy onsets. Since N pair states have been identified as important in recent studies of Ga(In)NAs,[10,11] to probe their significance in GaNSb, a three-level version of the BAC model is implemented which explicitly accounts for N pair states.

To this end, the band structure of GaN$_x$Sb$_{1-x}$ alloys was calculated using the methods developed by O'Reilly *et al.*[12,13] and Wu *et al.*[14] An example with $x = 0.015$ is shown in Fig. 3. In particular, the implementation is as described by Vogiatzis and Rorison,[10] with a many impurity Anderson model incorporating an impurity level associated with isolated N atoms, E_N, and one due to N-N second nearest neighbor pairs, E_{NN}, where a single Ga atom has two N neighbors. Each impurity level separately interacts with the host conduction band and the impurity levels do not interact with each other. At its simplest, this can be considered as a three level BAC model. However, within this approach, lifetime broadening can also be included by solving the Hamiltonian of the system using the Green's function coherent potential approximation approach, wherein the real and imaginary parts of the Green's function represent respectively the energy dispersion and broadening of the subbands.[10,14] Additionally, the host GaSb conduction band and its nonparabolicity are described by a (4×4) $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian that includes interactions of the GaSb conduction band with the valence bands. As a result, three conduction subbands with finite width can be seen and are denoted E_1, E_2 and E_3. The adjustable parameters in this model of the

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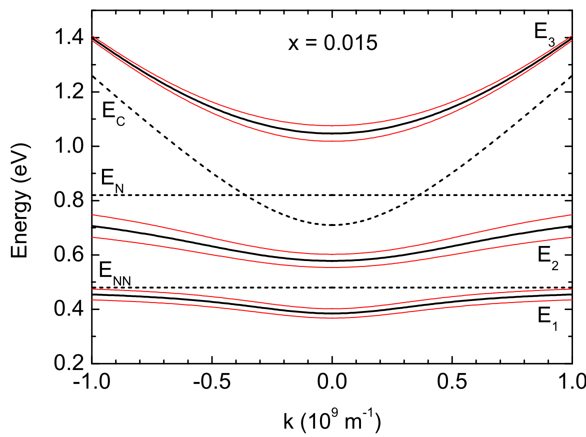

FIG. 3. Band structure close to the Γ point of the Brillouin zone for GaN_xSb_{1-x} with x = 0.015, calculated using the many impurity Anderson model, including the N pairs states and lifetime broadening. The narrow solid lines illustrate the broadening of the bands.

GaNSb band structure are the impurity level energies, E_N and E_{NN}, the BAC coupling matrix elements, $V_{MN} = \beta_N x_N^{1/2}$ and $V_{MNN} = \beta_{NN} x_{NN}^{1/2}$, and the broadening of the impurity levels, Δ_N and Δ_{NN}. 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 $x - 2x_{NN}$.

The conduction band density of states (DOS) calculated using this many impurity Anderson model is plotted in Fig. 4 as a function of N content. The lowest energy peak of the density of states is associated with the lowest subband, E_1, the second peak with E_2 and the onset feature with the highest E_3 subband. For the lowest N contents, the lowest peak is weak due to the low concentration of N pair states. This means that it does not contribute significantly to the observed absorption, explaining why the lowest absorption onset data points for $x = 0.0018$ and $x = 0.0031$ appear above the model curve in Fig. 2. The lowest energy model curve in Fig. 2 corresponds to the energy position of the lowest subband, but that subband does not contribute significantly to the absorption until its DOS is high enough.

The parameters used in the modeling were optimized to reproduce the experimentally determined evolution with N content of the band edge positions from the absorption onsets. The impurity levels, $E_N = 0.82$ eV and $E_{NN} = 0.48$ eV above the valence band maximum, were found to best reproduce the experimental results. These values are in broad agreement with the values calculated by Lindsay *et al.*, which included all the various types of N complexes, using tight binding supercell calculations.[15] By fitting to the high energy absorption onset values, the optimum value of β_N was found to be 2.4 eV, the same as obtained by Lindsay *et al.* Similarly, fitting to the low energy absorption onset values enabled β_{NN} to be determined to be 3.39 eV. This means that the pair state coupling to the conduction band is the expected $\sqrt{2}$ times higher than that for the isolated N states.[16] The addition here of an effective N pair level to the more widely used two level model can be considered to be the simplest model required to obtain agreement with the energy positions of the absorption onsets, without including all types of N complexes suggested in theoretical studies. The model presented here also refutes the earlier suggestion that the particularly low energy absorption edges observed from GaNSb alloys are associated with defect-induced valence band tails.

Comparing the calculated conduction band DOS plotted in Fig. 4 with the absorption spectra of Fig. 1(a) leaves one issue to be resolved of why the experimental absorption data exhibit just two onsets rather than a clear feature associated with each of the three conduction subbands. Specifically, for the curves corresponding to higher N contents in Fig. 4, a pronounced peak corresponding to the E_2 subband is evident, which does not appear in the absorption spectra of Fig. 1(a). In order to address this question, modeling of the absorption spectra has been performed. Since the many impurity Anderson methodology does not enable straightforward calculation of momentum matrix elements for each of the nine transitions (from the light hole, heavy hole, and split off valence bands to each of the conduction subbands, E_1, E_2, and E_3), an alternative method that neglects lifetime broadening has been applied. The absorption modeling approach of Perlin *et al.*,[17] extended to include N pair states, has been used to calculate the absorption spectra shown in Fig. 1(b). Within this approach, the absorption coefficient, α, is

$$\alpha(E) \propto \sum_{c,v} \frac{|P_{cv}|^2 g_{cv}(E)}{h\nu}, \tag{2}$$

where $g_{cv}(E)$ is the joint density of states, $h\nu$ is the incident photon energy, and P_{cv} are the momentum matrix elements for each of the nine transitions, derived for the three level BAC model by analogy with the approach used by Perlin *et al.* for the two level system.[17] The matrix elements P_{cv} are plotted for $x = 0.0163$ in Fig. 1(c) as a function of energy for the transitions from the light hole and heavy hole valence bands to the E_1, E_2, and E_3 conduction subbands. For GaSb, the split off valence band maximum is 0.76 eV below the light and heavy hole valence band maxima[9] and so the three transitions from the split off band to the conduction subbands do not contribute to the absorption spectra within the energy range shown, and the majority of their contribution is obscured by the large absorption above 1.4 eV by the GaAs substrate.

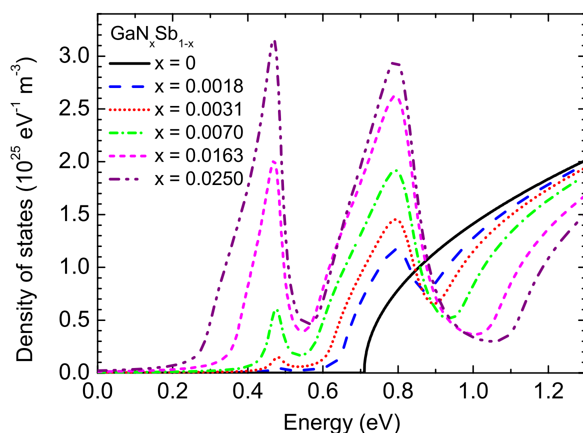

FIG. 4. Conduction band density of states for GaN_xSb_{1-x} with $0 \le x \le 0.0250$ calculated using the many impurity Anderson model, including the N pairs states and lifetime broadening.

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Within this model approach, the trends observed in the experimental absorption spectra are well reproduced. The absorption onsets are sharper in the model than the measured curves as a result of lifetime broadening being neglected. The lowest energy absorption onset versus N content from this model using the same parameters as given above is shown by the dotted line in Fig. 2 and exhibits a slightly sharper decrease than obtained before. The optimum fit to the measured onsets, for this model, is given by adjusting E_N to 0.83 eV and E_{NN} to 0.50 eV. The momentum matrix elements shown in Fig. 1(c) are lower at the onset for transitions to the E_2 subband than for the other two conduction subbands and also decrease with increasing energy. A similar trend for the momentum matrix elements in the lifetime broadened model would explain the lack of a distinct feature in the experimental absorption spectra associated with the E_2 peak in the DOS. An additional reason for the E_2 subband DOS peak not manifesting itself as a distinct absorption feature is that the pair level used here is effectively an average of a distribution of pair and cluster states, the presence of which act to further smear out the absorption spectra.

In conclusion, the band gap of GaN_xSb_{1-x} has been shown to decrease from 0.72 eV for GaSb to 0.30 eV for $x = 0.025$. The evolution of the low and high energy absorption edges has been reproduced by a three level BAC model within the many impurity Anderson approach employing the Green's function method incorporating lifetime broadening. Model absorption spectra that reproduce the essential features of the experimental data have also been calculated, again using the three level BAC model, but neglecting lifetime broadening. The N pair states strongly influence the conduction band dispersion leading to an initial rapid reduction of the band gap energy for small N contents ($x < 0.004$). Thereafter, the reduction of the band gap as a function of N content is less pronounced than previously suggested from two level BAC analyses. The absorption spectra and modeling presented here confirm theoretical predictions that the effects of N pair states are more pronounced in GaNSb than in GaNAs, for which the room temperature band gap versus N content is well reproduced by the two level BAC model.[18] This is due to the proximity of the pair states to the conduction band minimum in the GaNSb alloy.[15,19]

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