Band gap reduction in InNxSb1-x alloys: Optical absorption, k · P modeling, and density functional theory


Citation: Applied Physics Letters 109, 132104 (2016); doi: 10.1063/1.4963836
View online: http://dx.doi.org/10.1063/1.4963836
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/109/13?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Contactless electroreflectance and theoretical studies of band gap and spin-orbit splitting in InP1−xBix dilute bismide with x ≤ 0.034

Impact of cation-based localized electronic states on the conduction and valence band structure of Al1−x In x N alloys

Band gap tuning and optical absorption in type-II InAs/GaSb mid infrared short period superlattices: 14 bands K·p study

Full-zone k.p model for the electronic structure of unstrained GaAs1−x P x and strained Al x In1−x As alloys

From N isoelectronic impurities to N-induced bands in the GaN x As 1−x alloy

Pure Metals • Ceramics
Alloys • Polymers
in dozens of forms

Goodfellow
Small quantities fast • Expert technical assistance • 5% discount on online orders
Band gap reduction in InN$_x$Sb$_{1-x}$ alloys: Optical absorption, $k \cdot P$ modeling, and density functional theory


1Laboratory for Optical Spectroscopy of Nanostructures, Faculty of Fundamental Problems of Technology, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, Wroclaw, Poland
2Stephenson Institute for Renewable Energy and Department of Physics, School of Physical Science, University of Liverpool, Liverpool L69 7ZF, United Kingdom
3University College London, Department of Chemistry, London WC1H 0AJ, United Kingdom
4Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom
5Diamond Light Source Ltd., Didcot, Oxfordshire OX11 0DE, United Kingdom

(Received 29 April 2016; accepted 19 September 2016; published online 29 September 2016)

Using infrared absorption, the room temperature band gap of InSb is found to reduce from 174 (7.1 μm) to 85 meV (14.6 μm) upon incorporation of up to 1.13% N, a reduction of ~79 meV/%N. The experimentally observed band gap reduction in molecular-beam epitaxial InSb thin films is reproduced by a five band $k \cdot P$ band anticrossing model incorporating a nitrogen level, $E_N$, 0.75 eV above the valence band maximum of the host InSb and an interaction coupling matrix element between the host conduction band and the N level of $\beta = 1.80$ eV. This observation is consistent with the presented results from hybrid density functional theory. © 2016 Author(s).

In addition to band gap reduction, the Auger recombination rate for InNSb alloys has been suggested to be three times lower than that of comparable band gap HgCdTe alloys due to the high electron effective mass, which makes InNSb a promising material for long-wavelength light sources and photodetectors. However, in spite of continued interest in InNSb alloys over the last 15 years, straightforward optical spectroscopic evidence of the band gap reduction in samples of known N content has still not been reported and so reliable BAC parameters have not been determined.

In this letter, infrared absorption measurements of the band gap of epitaxial InSb thin films with nitrogen incorporation of up to 1.13% are presented, analyzed using the BAC model, and compared with the results of hybrid density functional theory (DFT). The band gap of InN$_x$Sb$_{1-x}$ alloys is shown to decrease from 174 meV (7.1 μm) for $x = 0$ to 85 meV (14.6 μm) for $x = 1.13$%, which corresponds to a band gap reduction of ~79 meV/%N. Simulations of the absorption, based on a joint density of states method, including the BAC interaction reproduce the experimental absorption spectra well. The band gap reduction as a function of N content is also well reproduced by the BAC model. The BAC matrix element coupling strength is estimated to be 1.80 eV, using a nitrogen level of 0.75 eV above the valence band maximum (VBM). These findings and preliminary low temperature absorption measurements are consistent with the hybrid DFT results. Overall, these results indicate that InNSb alloys are suitable for sources and detectors operating in the 8–14 μm atmospheric transmission window and

The substitution of highly electronegative nitrogen for a few percent of the host anions in III–V semiconductors is known to lead to a significant band gap reduction. Such dilute nitride III–V compounds have attracted attention in recent years due to realised device applications, including subcells in world record efficiency multi-junction solar cells, as in the years due to realised device applications, including subcells in nitride III-V compounds have attracted attention in recent years due to realised device applications, including subcells in nitride III-V compounds have attracted attention in recent years due to realised device applications, including subcells in nitride III-V compounds have attracted attention in recent years due to realised device applications, including subcells in...
provide the BAC parameters needed for modeling for understanding related quaternary alloys such as GaInNSb and InNSbBi and for future device design.

The InNSb epilayers were grown at the University of Warwick by N plasma assisted solid-source MBE on 100 nm InSb buffer layers on quarters of 51 mm diameter undoped InSb(001) substrates. Prior to growth, the N plasma was struck in a separate chamber with a power of 500 W and a flow rate of 0.2 sccm. The InNSb epilayers were grown to a thickness of ~400 nm at a fixed growth rate of nominally 0.5 µm h⁻¹ using substrate temperatures, determined by pyrometer, ranging from 270 to 365 °C. The surface morphology was investigated by atomic force microscopy (AFM) with an Asylum research MFP-3D microscope in tapping mode. The lattice constant of the InNSb films was determined using high resolution X-ray diffraction (XRD) using a Philips X’Pert diffractometer equipped with monochromatic Cu Kα1 X-ray source (λ = 0.15406 nm) with a four bounce Ge monochromator. XRD analysis was performed using the Panalytical X’pert Epitaxy application. AFM indicates the root mean square roughness values (uncorrelated with N content) in the range of 0.5–3.0 nm for all samples from 5 × 5 µm² images. There is no evidence from AFM measurements of any condensation of Sb on the films’ surface. Transmittance measurements were performed at room temperature using a Bruker Vertex 70V Fourier-transform infrared spectrometer, using a liquid nitrogen-cooled HgCdTe detector between 50 and 1200 meV. Additionally, transmissivity measurements were made in the temperature range 4–300 K for a film with 0.73% N content using a continuous-flow He cryostat.

The incorporation of N in InSb has also been investigated using DFT calculations employing hybrid functionals which often provide better structural data and more accurate band gaps than the local density and generalized gradient approximations.25–29 Here, the screened HSE06 (Heyd-Scuseria-Ernzerhof) hybrid density functional is used,30 as implemented in the Vienna Ab initio Simulation Package (VASP).31–33 The value of exact nonlocal exchange, x, was 31.0%, which gives a band gap of 231 meV for InSb, in good agreement with the 0 K band gap of 235 meV extrapolated from the low temperature experimental data.34 The valence–core interaction was described using the projector augmented wave (PAW) approach,35 and cores of [Kr] for indium and antimony and [He] for nitrogen are used. A cutoff of 400 eV was used for all the calculations, with the Brillouin zone sampled employing a 8/C2/C2/C2 expansion of the 8 atom cubic cell (i.e., a 64 atom supercell), corresponding to an N concentration of 3.125%. This supercell size has been shown to be well converged when modeling N in other III–V materials.36,37 Geometry optimisation was deemed to have converged when the forces on all the atoms were less than 0.01 eV Å⁻¹. The band structure of the supercell containing one N was unfolded to the primitive cell band structure using the BandUP code.38,39 All the calculations included spin-orbit coupling, which, for bulk InSb gives a spin-orbit valence band split off of 800 meV, in good agreement with experiment (803 meV).40

The N fraction was determined for epilayers grown at temperatures between 270 and 365 °C using a fixed growth rate of 0.5 µm h⁻¹. Both the N fraction and the epilayer thickness were determined by XRD, where both the 004 peak splitting and the Pendellösung fringes were modeled by dynamical simulations. The epilayer peak occurs at higher Bragg angle than the substrate peak, corresponding to the InNSb layer having a smaller lattice parameter than that of InSb. The N content was determined under the assumption that Vegard’s law is valid using an endpoint lattice parameter for zinc blende InN of 5.01 Å.41 Example measurements and simulations are shown in Fig. 1 for layers with 1.13 and 0.73% of their Sb sublattice substituted by N atoms. (The sample with 0.73% N was grown in a separate growth run from the others in order to fill the composition gap between 0.54% and 1.1% N. By the time of the later growth run, the N plasma source aperture plate had been modified and so, to fill the composition gap, the sample was grown at 275 °C but at a higher growth rate of 1.75 µm h⁻¹.) The N content from XRD (for fixed N plasma source conditions and fixed growth rate) increases as the growth temperature decreases and begins to reach a plateau corresponding to x = 1.14% for growth temperatures below approximately 270 °C (see Fig. S1 of supplementary material). These results are similar to those of Zhang et al. who grew InNSb at between 250 and 350 °C.42 The temperature dependence of the N incorporation in InN0.4Sb0.6 has been modeled using the kinetic approach of Wood et al.43 and Pan et al.,44 which has previously been applied to N incorporation in GaNSb and GaInNSb alloys.45,46 The curve shown in Fig. S1 is a very good fit to the experimental data and corresponds to an energy barrier for loss of N of 1.79 eV and a characteristic surface residence lifetime of N atoms of 5 µs. For comparison, the previously reported equivalent values for GaNSb are 2.0 eV and 5 µs.45 This lower energy barrier is consistent with the

![FIG. 1. XRD (points) of the 004 diffraction maximum from the InNSb films grown on an InSb substrate at 275 °C at growth rates of 0.5 and 1.75 µm h⁻¹. The results of the simulations (solid line) indicate that the InNSb films contain 1.13 and 0.73% N and their thickness are 390 ± 10 nm and 400 ± 10 nm, respectively.](image-url)
requirement to grow InSb at a lower temperature than GaSb for N incorporation.

The band structure close to the Γ point of In$_{x}$N$_{0.01}$Sb$_{0.99}$ alloys was calculated using the k·P BAC model. The dispersion of the $E_{\pm}$ subbands can be determined by finding the eigenvalues of the $2 \times 2$ determinant

$$
\begin{vmatrix}
E_c(x) - E & \beta \sqrt{x} \\
\beta \sqrt{x} & E_N(x) - E
\end{vmatrix} = 0,
$$

(1)

where $E_c(x) = E_{c0} - \alpha x$ and $E_N(x) = E_{N0} - \gamma x$ are the assumed energies of the conduction band edge and isolated N level with respect to the InSb valence band maximum (VBM). The values $\alpha = 2.44$ eV and $\gamma = 2.47$ eV are taken from fitting to previous tight binding results. The $x$-dependence of the effective N level is due to interactions with other N-related states, such as different N pair and cluster configurations that are more likely to occur as the N content, $x$, increases. The value of $\beta$ is determined by fitting to the experimental data. Within this model, the host InSb conduction band and its nonparabolicity are described by Pidgeon and Brown’s $(4 \times 4)$ k·P Hamiltonian that includes interactions of the InSb conduction band with the valence bands and the influence of higher lying bands. So this results in a $(5 \times 5)$ Hamiltonian (or $(10 \times 10)$ if spin degeneracy is included) to describe the InNSb. As a result of the interaction of the nitrogen level with the host conduction band, two conduction subbands form and are denoted as $E_{+}$ and $E_{-}$. An example with $x = 1\%$ is shown in Fig. 2.

The optical properties of the InNSb epilayers as a function of N content were studied using transmission measurements. The transmission data from each sample were divided by the transmission from a different quarter of the same InSb wafer so that the remaining signal corresponds to transmission through the InNSb layer. This ratioing of the sample data with data from an InSb substrate accounts for the decrease in $\Delta \alpha$ above the band gap of the InSb—the absorption of InNSb converges to that of InSb as $E_{+}$ approaches the InSb conduction band (see Fig. 2). The absorption spectra calculated from the transmission data for the samples with $x = 0.54\%$, $0.73\%$, and $1.1\%$ are shown in Fig. 3(a). The band gap red shifts with increasing N content. The absorption edge decreases in energy to $85 \pm 15$ meV as the N content is increased to $x = 1.13\%$, corresponding to a wavelength of $\sim14.6 \mu$m. This corresponds to a band gap reduction of $79 \pm 5$ meV/\%N. Model absorption curves are shown in Fig. 3(b). The approach of Perlin et al. has been used to calculate the model absorption spectra. Accordingly, the absorption coefficient, $\alpha$, is

$$
\alpha(E) \propto \sum_{\mathbf{k},\mathbf{p}} |P_{\mathbf{k}}|^2 g_{\mathbf{k}}(E) / h\nu,
$$

(2)

where $g_{\mathbf{k}}(E)$ is the joint density of states, $h\nu$ is the incident photon energy, and $P_{\mathbf{k}}$ are the momentum matrix elements for the optical transitions, derived from the BAC model. Here, the calculated absorption of InSb was subtracted from the calculated absorption spectrum of In$_{x}$N$_{0.01}$Sb$_{0.99}$ which is equivalent to ratioing the transmission data. 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 experimental absorption edge as a function of N content is shown by the open circles in Fig. 4. The BAC model well reproduces the trend of the band gap reduction, which is determined by the transition between the VBM and the minimum of the $E_{-}$ subband, which is shown by the thick solid line in Fig. 4. Within the BAC model, the adjustable parameters of the InNSb band structure are the energy of the N impurity level, $E_{N}$, and the BAC coupling strength, $\beta$, in the coupling matrix element, $V_{MN} = \beta \sqrt{x}$. The N level is set to 0.75 eV above the VBM, according to the results of previous tight binding calculations. The optimum fit is then

![FIG. 2. (a)](image-a)

![FIG. 3. (a)](image-b)
dependence on N content has been calculated using the bands, $E_-$ and $E_+$, are shown in inset in Fig. 4. The band dispersions from $\mathbf{k} \cdot \mathbf{p}$ calculations are also shown. Without significantly changing the band dispersions, the value of $\beta$ in the $\mathbf{k} \cdot \mathbf{p}$ was adjusted from 1.80 to 1.65 eV to reproduce the DFT band gap for $x = 3.125\%$. The $\mathbf{k} \cdot \mathbf{p}$ dispersions match those from hybrid DFT for the topmost valence band and the $E_-$ subband. The energy position of the $E_+$ band is similar for both methods, but with flatter dispersion in the $\mathbf{k} \cdot \mathbf{p}$ results.

The band gap reduction of 79 meV/%N represents a large proportional change due to the small band gap of InSb, but is about half the absolute band gap change per %N compared with that seen in GaNAs alloys (150 meV%). This is a consequence of the N level lying more than 550 meV above the CBM in InNSb compared with only 250 meV for GaNAs. The InNSb band gap reduction per %N is greater than twice that observed per %Bi in InSbBi alloys (35 meV%Bi), but is accompanied by much greater lattice parameter change due to the greater difference between the zinc blende InN and InSb lattice parameters compared with that of the zinc blende InBi and InSb parameters. Additionally, the InNSb calculation suggests that at room temperature band gap closure will occur for $x > 2.3\%$, giving a semimetallic band structure. Some circumstantial evidence of such band gap closure has previously been reported by Veal et al. at low temperature (0 or 4 K), band gap closure is predicted to occur at or greater than 3% N.

See supplementary material for figures showing N content from XRD versus growth temperature along with kinetic modeling and also the absorption spectra recorded at 4 K from an InSb substrate and from InNSb/InSb with 0.73% N.

The experimental work was supported by the Engineering and Physical Sciences Research Council (EPSRC) under Grant No. EP/G004447/2. W.M.L. acknowledges support from the National Science Center (NCN) Grant No. 2014/13/D/ST3/01947. D.O.S. and T.D.V. acknowledge support from the Materials Design Network. J.B. and C.R.A.C. acknowledge funding from the EPSRC Grant No. EP/K016288/1. The hybrid DFT was performed on the supercomputer ARCHER via funding from the EPSRC Grant No. EP/L000202/1.

FIG. 4. The room temperature (300 K) band gap versus N content determined from the absorption spectra for the InN$_{x}$Sb$_{1-x}$ samples with $0 < x < 1.13\%$ (open red circles) and calculated composition dependence of the band gap of InN$_{x}$Sb$_{1-x}$ using the $\mathbf{k} \cdot \mathbf{p}$ BAC model (thick solid red line). The hybrid DFT band gaps (0 K) for InSb and InNSb with 3.125% N are also shown (closed blue circles) and joined by a dotted blue line. The 4 K experimental band gaps from optical absorption of InSb and InNSb with 0.73% N are also shown (open blue squares). The thin solid blue line is the band gap variation for 4 K using the $\mathbf{k} \cdot \mathbf{p}$ BAC model and the dashed blue line is from the same model but with a fixed effective N level, equivalent to removing the effect of N pairs and clusters. Inset is the $\Gamma$ to X direction band dispersions of the highest valence band (the heavy hole valence band) and the two lowest conduction bands (the $E_-$ and $E_+$) subbands from hybrid density functional theory (points) and the $\mathbf{k} \cdot \mathbf{p}$ modeling (solid lines).