Growth and Characterisation of Dilute Antimonide Nitride Materials for Long Wavelength Application

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Abstract

The addition of small amounts of nitrogen to III-V semiconductors leads to a large degree of band-gap bowing, giving rise to band-gaps smaller than in the associated binary materials. The addition of a small percentage of nitrogen to GaSb or InSb is predicted to move their response wavelengths into the long or even very long wavelength IR ranges. We report the growth of GaN_xSb_{1-x} and InN_xSb_{1-x} by MBE, using an r.f. plasma nitrogen source, examining the influence of plasma power, substrate temperature and growth rate. We demonstrate high structural quality, as determined by x-ray diffraction, and FTIR absorption measurements show a shift in the cut-off wavelength to over 3 μm for GaNSb and over 11 μm for InNSb, accounting for the competing effect of Moss-Burstein band filling.

Keywords: Dilute nitride, indium antimonide, InSb, gallium antimonide, GaSb, infrared, MWIR, LWIR

Introduction

The addition of small amounts of nitrogen to III-V semiconductors leads to a large degree of band-gap bowing, giving rise to band-gaps smaller than in the associated binary materials[1]. In particular, dilute arsenide nitrides such as GaN_xAs_{1-x} and $Ga_{1-y}In_yN_xAs_{1-x}$, have recently received much attention. The substitution of nitrogen onto a few per cent of the arsenic sites has been shown to reduce the band-gap and lattice constant, allowing GaInNAs alloys to be produced that respond in the optical fibre wavelength range of 1.3 to 1.55 μm and are lattice matched to GaAs[1-4].

The band-gap reduction due to the localised interaction between the host conduction band and the resonant level, which arises from the substitution of highly electronegative nitrogen for a few percent of the host anions[5,6], can be described by the band anti-crossing (BAC) model[5]. The electronegativity mismatch between nitrogen and antimony is greater than for any other combination of commonly used group V elements, consequently the band-gap reduction in dilute antimonide nitrides is expected to be more extreme than for dilute arsenide nitrides, such that the addition of a small percentage of nitrogen to GaSb or InSb is predicted to move their response wavelengths into the long or even very long wavelength IR ranges, as shown in Figure 1.

The dilute III-antimonide nitrides have several potential advantages compared with alternative materials that are sensitive in the mid and long IR wavelength ranges. For example, compared with type-II superlattices, they do not have an InAs component so passivation is easier, and compared with mercury cadmium telluride (MCT), uniformity should be more

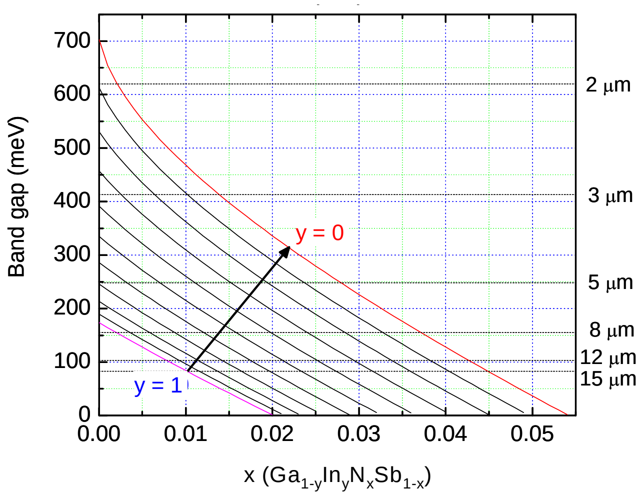

Figure 1. Calculated band-gap (left hand axis) and cut-off wavelength (right hand axis) of $Ga_{1-y}In_yN_xSb_{1-x}$ vs. nitrogen composition for values of In composition ranging from 0% to 100% in 10% increments.

controllable. Furthermore, there is a theoretical indication that electron effective mass is higher, so diode junction breakdown through tunnelling may be suppressed, which would be particularly important for very long wavelength IR (VLWIR) detection. Finally, as the addition of nitrogen to GaSb decreases the lattice constant, whereas indium increases it, $Ga_{1-y}In_yN_xSb_{1-x}$ offers the prospect of lattice matched growth onto GaSb or InAs substrates for multi-band III-V detectors. Hence these materials offer a very exciting addition to the range of options for materials for high performance infrared detectors, which has stimulated this study into their basic feasibility.

We report the growth of GaN_xSb_{1-x} and InN_xSb_{1-x} by molecular beam epitaxy (MBE), using an r.f. plasma nitrogen source, examining the influence of plasma power, substrate temperature and growth rate. The structural quality of the layers is tested by X-ray diffraction (XRD) and their optical properties investigated using Fourier Transform Infra-red (FTIR) absorption spectroscopy. Single field Hall measurements are used to determine the electrical properties of the layers.

Growth and structural characterisation

The material has been grown by MBE, using techniques described previously[7]. Standard effusion cells were used for Ga, In and Sb_4. The active nitrogen was supplied by an Oxford Applied Research HD25 plasma source. Thin (~ 250 nm) GaN_xSb_{1-x} and InN_xSb_{1-x} layers were grown onto undoped GaSb(100) and InSb(100) substrates respectively, for characterisation by XRD. Thicker (2 μm) dilute nitride layers were grown onto semi-insulating GaAs(100) substrates for characterisation by Hall effect measurement and FTIR spectroscopy[8]. The use of an insulating substrate that also has a much larger band-gap than the dilute nitride alloys allows the electrical and optical properties to be investigated without being affected by substrate conduction or optical absorption in the wavelength range of interest. The double crystal X-ray diffraction (DCXRD) was performed, using the symmetric (004) reflection in a Philips diffractometer with Cu Kα radiation (λ = 0.15406 nm), and compared with simulated spectra.

A range of growth conditions was explored by varying the growth temperature, plasma power, growth rate and Sb overpressure. The variation in nitrogen composition of GaN_xSb_{1-x} obtained as a function of growth temperature for various values of plasma power is shown in Figure 2.

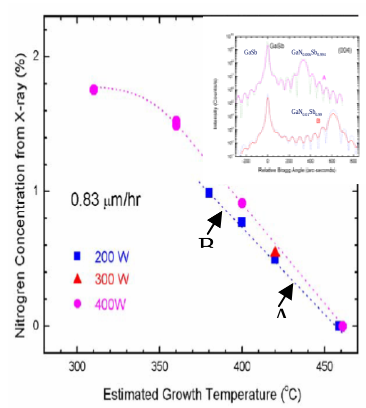

Figure 2. GaNSb nitrogen composition vs. growth temperature for various values of plasma power and, inset, example DCXRD plots for 2 different nitrogen concentrations (as labelled).

It can be seen that for a fixed chamber pressure and plasma power, decreasing the growth temperature from 460°C to 310°C increased the nitrogen incorporation from virtually zero to 1.75%, as determined from DCXRD. The nitrogen plasma power, however, had comparatively little effect on the amount of nitrogen incorporated. All of the DCXRD spectra showed a similar, high crystalline quality, as shown in Figure 2, except for the lowest temperature (310°C), where weaker fringes were observed, possibly indicating that the lower bound for the growth temperature window, under these conditions, is approximately 300°C. The variation in nitrogen incorporation was also investigated as a function of growth rate. A trend of increasing nitrogen concentration with increasing growth rate was observed, which is counter to that observed for the dilute arsenides[9] and suggests that the incorporation is mediated by a different mechanism to the simple availability of nitrogen. The possibility of Sb acting as a surfactant and preferentially incorporating nitrogen at higher growth rates was investigated by varying the Sb overpressure. However no correlation was

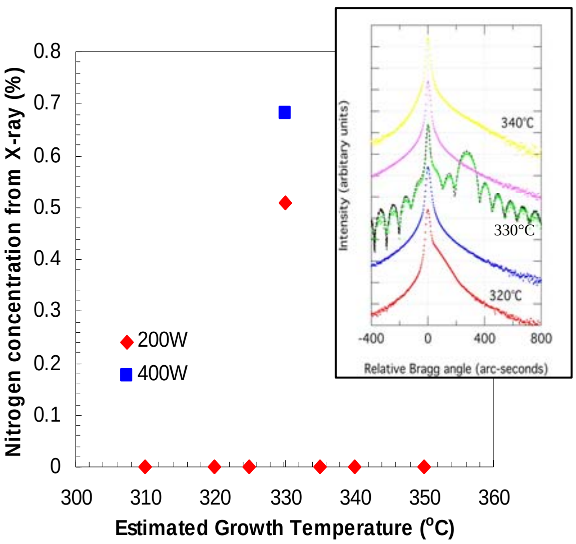

Figure 3. InNSb nitrogen composition vs. growth temperature for v values of plasma power and, inset DCXRD plots showing good structural quality at T_g = 330°C.

observed and further work is required to explain the trend.

The growth of InN_xSb_{1-x} was studied as a function of growth temperature and plasma power. The results, shown in Figure 3, indicate a very narrow (~5°C) temperature window in which good structural quality, nitrogen containing material can be grown.

The very narrow growth temperature window may be due to two competing mechanisms controlling nitrogen incorporation and it may be that by increasing the Sb activation through the use of a cracker cell that this window can be widened.

Electrical and optical characterisation

Single field Hall measurements have been performed and show the GaN_xSb_{1-x} and InN_xSb_{1-x} material to have p-type and n-type carrier concentrations in the 10^{18} cm^{-3} range respectively. These carrier concentrations are invariant with nitrogen content and show little freeze-out at 77K. GaSb and InSb material grown under equivalent conditions has carrier concentrations in the 10^{15} cm^{-3} range and shows little evidence of damage from non-nitrogen containing plasma (i.e. from exposure to Ar plasma). It is therefore clear from dilute nitride material showing a high carrier concentration but little nitrogen that is active in changing the lattice constant (from DCXRD), that substantial amounts of nitrogen are incorporating interstitially or on antisites and having a detrimental effect on the electrical properties of these materials.

The room temperature (RT) FTIR absorption spectra of GaN_xSb_{1-x} and InN_xSb_{1-x} have been recorded and compared with the spectra for GaSb and InSb respectively.

The band-gap of the GaN_xSb_{1-x} layers was estimated by extrapolation of the linear region of the α^2E^2 (where α is the absorption coefficient and E is the photon energy) curve down to the base line, see Figure 4. The band-gap of the GaSb control layer was determined to be 720±10 meV, in close agreement with the literature value of 726 meV.

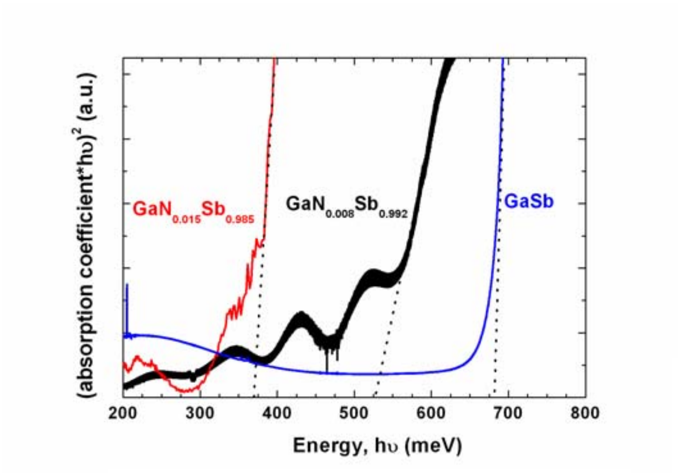

Figure 4. Absorption spectra for 2 different N containing GaN_xSb_{1-x} layers compared with a GaSb layer spectrum.

The absorption edge is seen to move to significantly lower energies for the two GaN_xSb_{1-x} layers. The higher nitrogen content layer, x = 0.015, shows a band-gap of 380±20 meV, giving a reduction of approximately 340 meV compared with GaSb and corresponding to a cut-off wavelength of 3.3 µm. For comparison, the incorporation of 1.5% nitrogen in GaAs results in a reduction in the band-gap of 220 meV[6]. This confirms that the larger electronegativity mismatch between nitrogen and antimony, than between nitrogen and arsenic, produces a greater reduction in band-gap for a given nitrogen substitution.

RT FTIR absorption spectra of the InN_xSb_{1-x} material are shown in Figure 5. The band gap of the InSb control layer was determined to be 200±20 meV, in reasonable agreement with the literature value of 170 meV. However the spectra show the absorption edge for InN_xSb_{1-x} moving to higher energies compared to InSb. This disagreement with the theoretical prediction of the band-gap energy (see Figure 1) can be explained by considering the influence of the high carrier concentration. The position of the InN_xSb_{1-x} absorption edge (E_α) is a summation of the three effects shown in equation 1,

$$E_\alpha = E_g + E_{MB} - E_{BGR} \qquad (1)$$

E_g is the material band-gap, which is reduced upon nitrogen incorporation. E_{MB} is the Moss-Burstein band filling effect and E_{BGR} the band-gap renormalisation both of which result from the high carrier concentrations in these samples. These effects are well documented in optical absorption studies of InNAs[10].

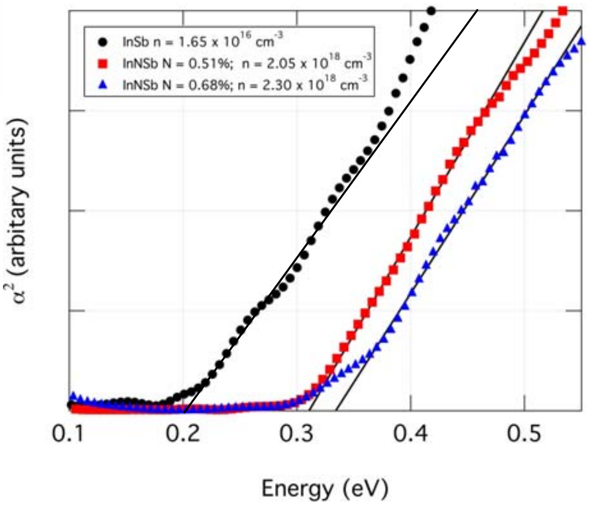

Figure 5. Absorption spectra for 2 different N containing InN_xSb_{1-x} layers compared with an InSb layer spectrum.

Nitrogen (%)	E_g (meV)	E_{MB} (meV)	E_{BGR} (meV)	E_α calc. (meV)	E_α expt. (meV)
0.51	128	222	20	330	310
0.68	112	240	20	332	330

Table 1. Theoretical prediction of absorption edge for the InN_xSb_{1-x} layers shown in Figure 5.

Theoretical modelling of the InN_xSb_{1-x} band structure[11] indicates the expected adsorption edge for both samples in Figure 5 to occur at ~330 meV, as summarised in Table 1, and in reasonable agreement with the measured data. It can therefore be inferred that for InNSb containing 0.68% nitrogen, the band-gap has been reduced by over 50 meV compared with InSb and the cut-off wavelength has shifted to ~11 μm.

Conclusions

We have shown that nitrogen can be incorporated into GaSb (up to 1.5%) and InSb (up to 0.7%) grown by MBE, by use of an r.f. nitrogen source. X-ray diffraction measurements have shown both materials to have an excellent crystalline quality. Optical absorption measurements have demonstrated a band-gap reduction of more than 300 meV for GaNSb, corresponding to a shift in the cut-off wavelength to over 3 μm. The band-gap reduction for InNSb is complicated by the competing effect of Moss-Burstein band filling however a reduction of more than 50 meV can be inferred, corresponding to a shift in the cut-off wavelength to over 11 μm. Hall effect measurements have shown both GaNSb and InNSb to have high as-grown carrier concentrations and in order to realise devices using these narrow band-gap materials the free carrier concentration must first be dramatically reduced.

References

1. M. Weyers, M. Sato and H. Ando, Jpn. J. Appl. Phys., **31**, L853-L855 (1992)
2. H. Naoi, Y. Naoi and S. Sakai, Solid-State Electron., **41**, 319-321 (1997)
3. K. Uesugi, N. Morooka and I. Suemune, Appl. Phys. Lett., **74**, 1254-1256 (1999)
4. W. Shan, W. Walukiewicz, K. M. Yu, J. W. Ager, E.E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, S. R. Kurtz and C. Nauka, Phys. Rev., B 62, 4211-4214 (2000)
5. W. Shan, W. Walukiewicz, K. M. Yu, J. W. Ager, E.E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, S. R. Kurtz and C. Nauka, Phys. Rev. Lett., **82**, 1221-1224 (1999)
6. J. Wu, W. Shan and W. Walukiewicz, Semicond. Sci. Technol., **17**, 860-869 (2002)
7. T. Ashley, L. Buckle, G. W. Smith, B. N. Murdin, P. H. Jefferson, L. F. J. Piper, T. D. Veal and C. F. McConville, Proc. SPIE, **6206**, 62060L (2006)
8. L. Buckle, B. R. Bennett, S. Jollands, T. D. Veal, N. R. Wilson, B. N. Murdin, C. F. McConville and T. Ashley, *Proc. 13th Int. Conf on Molecular Beam Epitaxy, Edinburgh, UK, 2004,* J. Crystal Growth, **278**, 188-192 (2005)
9. M. Kondow and T. Kitatani, Semicond. Sci. Technol., **17**, 746-754 (2002)
10. T. D. Veal, L. F. J. Piper, P. H. Jefferson, I. Mahboob, C. F. McConville, M. Merrick, T. J. C. Hosea, B. N. Murdin, M. Hopkinson, Appl. Phys. Lett., **87**, 182114 (2005)
11. P. H. Jefferson, L. Buckle, D. Walker, T. D. Veal, S. Coomber, P. A. Thomas, T. Ashley, C. F. McConville, Phys. Stat. Sol (RRL), **3**, 104-106 (2007)

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