AIP | Applied Physics Letters

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Citation: Applied Physics Letters **95**, 031110 (2009); doi: 10.1063/1.3187534
View online: http://dx.doi.org/10.1063/1.3187534
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/95/3?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **95**, 031110 (2009)

Growth and characterization of InAsN/GaAs dilute nitride semiconductor alloys for the midinfrared spectral range

M. de la Mare,[1,a)] Q. Zhuang,[1] A. Krier,[1] A. Patanè,[2] and S. Dhar[3]
[1]*Department of Physics, Lancaster University, Lancaster LA1 4YB, United Kingdom*
[2]*School of Physics and Astronomy, Nottingham University, Nottingham NG7 2RD, United Kingdom*
[3]*Department of Electronic Science, University of Calcutta, 92 A. P. C. Road, Kolkata 700009, India*

(Received 3 March 2009; accepted 28 June 2009; published online 22 July 2009)

We report the growth of InAsN onto GaAs substrates using nitrogen plasma source molecular beam epitaxy. We describe the spectral properties of InAsN alloys with N-content in the range of 0%–1% and photoluminescence emission in the midinfrared spectral range. The photoluminescence emission of the sample containing 1% N reveals localized energy levels resonant with the conduction band states of InAsN. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3187534]

The addition of small amounts ($<1\%$) of nitrogen into narrow gap III-V compound semiconductors such as GaAs and InAs has been found to substantially reduce the band gap and also results in a large band gap bowing,[1–5] giving rise to interesting physical phenomena and holding great potential for the development of innovative technologies. The incorporation of N can increase the electron effective mass and equalize the density of states, thus reducing Auger recombination and inter valence band absorption processes, which currently limit the quantum efficiency of midinfrared light sources. InAsN is also an attractive alternative to other midinfrared materials, such as HgCdTe, PbSnTe, and InAsSb. Epitaxial growth of InAs based materials onto semi-insulating GaAs substrates is an attractive proposition since it provides effective isolation and transparency for the fabrication of light emitting diodes or detector arrays. However, the large lattice mismatch ($\sim 7\%$) (Refs. 6 and 7) results in the formation of extensive defects and dislocations, which have been found to act as efficient traps and recombination centers, thus degrading the optical quality of the epitaxial material.[8,9] In this paper, we report the growth of InAsN epilayers on (001) GaAs substrates using nitrogen plasma source molecular beam epitaxy (MBE) and with tunable photoluminescence (PL) emission in the mid-IR wavelength range.

All the InAsN layers were grown on semi-insulating (100) GaAs substrates obtained from Wafer Technology, Ltd. The preparation and oxide desorption in the growth chamber was carried out in the conventional manner.[10] InAsN epitaxial layers ~ 1 μm in thickness were grown at a growth temperature T_G in the range of 400–440 °C using a VG-V80H MBE reactor with a radio frequency nitrogen plasma source. A growth rate of 1 μm/hr was employed using an As-flux of 2×10^{-6} mbar. For the N-plasma source, a power $P = 160$ W and a N-flux of 5.0×10^{-6} mbar were used. The surface reconstruction was monitored by *in situ* reflection high energy electron diffraction, while the substrate temperature was measured using an infrared pyrometer calibrated with the surface reconstruction transitions at a fixed As-flux.

PL measurements were performed on all layers over the temperature (T) range of 4–300 K using an Oxford Instruments variable temperature continuous flow He cryostat. An Ar^+ ion laser (514 nm, with maximum power density of 20 W cm^{-2} at the sample) was used for excitation. The emitted radiation was collected using CaF_2 lenses and focused into a 0.3 m Bentham M300 monochromator. The radiation was detected using a cooled (77 K) InSb photodiode detector and a Stanford Research (SR850) digital lock-in amplifier. High resolution x-ray diffraction measurements using a Bede QC200 diffractometer confirmed a relaxation of 98% in the ~ 1 μm thick InAsN layers. The samples were found to contain between 0% and 1% N based on the Vegard's law assumption.[11]

Figure 1 shows the low temperature ($T = 4$ K) PL spectra for each of the as-grown InAsN epilayers on GaAs along with that obtained from an InAs reference sample. The PL emission from the different samples extends across the midinfrared (2–5 μm) spectral range. With increasing N-content the PL emission shifts to longer wavelengths in good agreement with previous reports on InAsN epilayers grown on different substrates.[12–15] Although InAs can be grown on GaAs (Refs. 16–18) using MBE, the large lattice mismatch ($\sim 7\%$) normally leads to completely relaxed layers with poor optical quality. The addition of N would be expected to further degrade the material. However, we found that the incorporation of N in InAs tends to increase the

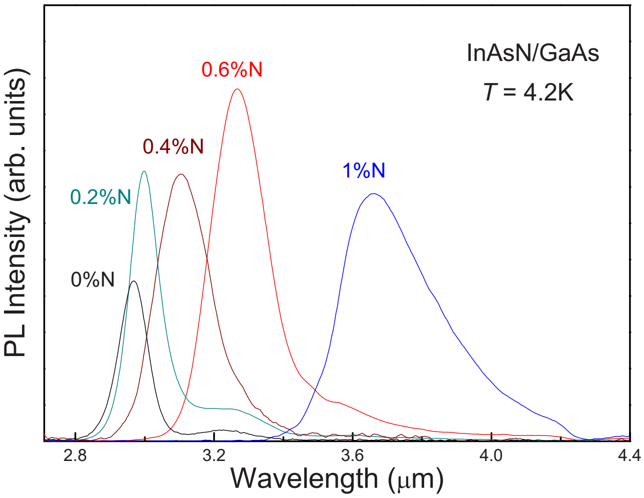

FIG. 1. (Color online) Low temperature ($T = 4$ K) PL emission spectra of InAsN and InAs reference samples grown on GaAs (001).

[a)] Electronic mail: m.delamare@lancaster.ac.uk.

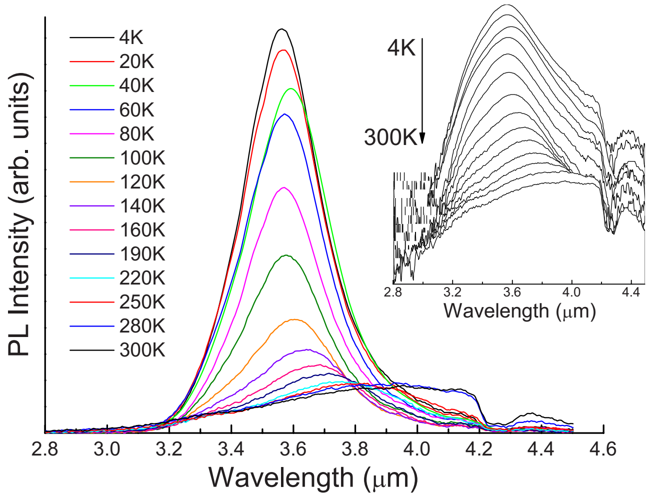

FIG. 2. (Color online) Temperature dependence of the PL spectrum for sample A0299 (1% N). The inset shows the semilog plot of the PL spectra. For clarity, the PL spectra in the inset are displaced along the vertical axis.

intensity of the PL emission. This phenomenon, which merits further investigation, may be related in part to the shift of native defect states into the conduction band as the nitrogen content increases. Also the N-incorporation could lead to an increase in the conduction band effective mass[19] leading to some equalization in the density of states, which would increase radiative recombination and also reduce nonradiative Auger processes.[20,21]

Figure 2 shows the temperature dependence of the PL emission for the InAsN sample with 1% N (sample A0299). The thermal quenching of the PL intensity is significantly weaker compared to that observed for InAs and a PL emission can be observed at room temperature, extending beyond 4.0 μm. At $T=4$ K, the PL emission is peaked at around 3.6 μm. With increasing temperature, the PL spectrum shifts to longer wavelengths and exhibits a pronounced broadening at $T>190$ K. Also note that as the temperature increases above $T=190$ K, a new PL feature becomes clearly visible at around 3.3 μm, at short wavelengths relative to the main PL peak. To reveal this feature more clearly, in the inset of Fig. 2 we plot a semilog plot of the temperature dependence of the PL spectra and in Fig. 3 we show the PL spectra after subtraction of an exponential fit to the high energy tail of the PL emission. This tail accounts for a thermal distribution of carriers and is well described by a dependence of the type $\exp(-h\nu/k_BT)$, where T is the lattice temperature and $h\nu$ is the photon energy.

As shown in Fig. 4, at low temperatures ($T<80$ K) the energy position of the PL emission deviates from the temperature dependence of the band gap[22] and reveals a distinct "S" shape behavior. This is characteristic for a PL emission involving carrier recombination from localized states and indicates a thermally activated redistribution of carriers between these states.[23,24] With increasing T, carriers trapped in the localized states overcome energy barriers and are thermally excited into the conduction band. Hence at high T, the PL emission is then primarily due to band-band recombination. Above 80 K the PL peak emission energy tends to follow the empirical Varshni equation,[22]

$$E_g(T)=E_g(0)-\alpha T^2/(T+\beta), \qquad (1)$$

where $E_g(0)$ is the energy gap at $T=0$ K, and α and β are the corresponding thermal coefficients. For InAs, $E_{g0}=415$ meV, $\alpha=0.276$ meV/K, and $\beta=83$ K.[25] We use Eq. (1) to describe the T-dependence of the energy, E, of the PL emission after subtracting from E a term $\frac{1}{2}k_BT$ to account for the thermal distribution of carriers.[26,27] The fit to the measured PL peak energies by Eq. (1) are $E_g(0)=355$ meV, $\alpha=0.25$ meV/K, and $\beta=110$ K, thus indicating a redshift of the band gap of 60 meV for 1% N and a T-dependence of the band gap that is weaker than in InAs.

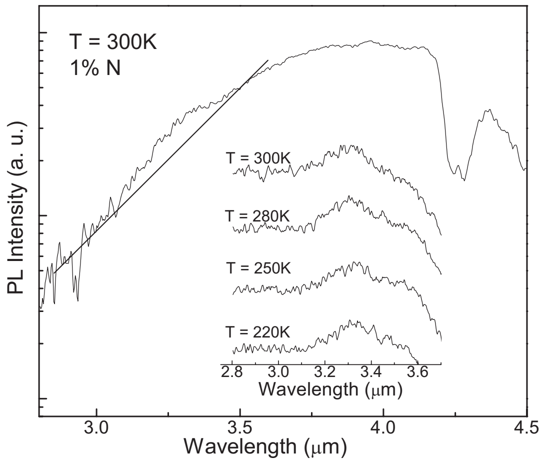

FIG. 3. PL spectrum at $T=300$ K for A0299 containing 1% N. The line is an exponential fit to the high energy tail of the PL spectrum. The inset shows the PL spectra at different T after subtraction of an exponential fit to the high energy side of the PL emission.

To explain the broadening of the PL spectrum at $T>190$ K and the corresponding appearance of an additional PL feature at ~3.3 μm (Figs. 2 and 3), we should consider several mechanisms. Hall Effect measurements have shown a relatively large residual electron concentration in this sample, i.e., $n_e=2\times10^{17}$ cm^{-3}, such that the InAsN behaves as a degenerate semiconductor. The broadening of the PL emission with increasing temperature is partly due to the thermal distribution of carriers around the Fermi energy. The form and T-dependence of the PL spectrum of a degenerate semiconductor can be also affected by Fermi edge singularity effects.[28,29] These were observed previously in highly n-doped InAs with carrier concentrations of ~3

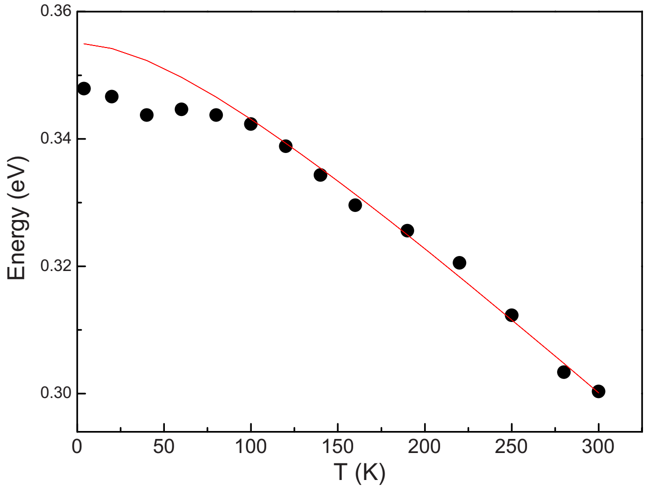

FIG. 4. (Color online) T-dependence of the PL peak energy for A0299 containing 1% N. The continuous line is the calculated T-dependence of the band gap energy according to the empirical Varshni equation.

$\times 10^{17}$ cm^{-3}. However, we note that these effects are normally more noticeable at low temperatures. In contrast, the broadening of the PL emission and the emergence of a new PL emission on the high energy side of the main PL band occurs at high T ($T > 190$ K). Interestingly, the wavelength position (~ 3.3 μm) of the additional PL feature is weakly affected by temperature over an extended temperature range ($T = 250 - 300$ K), thus suggesting the existence of localized energy levels that are resonant with the conduction band states of InAsN. We note that N–N pairs in InAs are expected to be high in energy relative to the conduction band minimum (>1 eV).[30] Therefore, other defects could be responsible for this unusual PL emission, such as N-clusters with lower energies and/or native defects that shift into the conduction band due to the N-incorporation. At low temperatures electrons do not have enough energy to occupy these resonant levels in the conduction band, but as the temperature rises electrons can gain enough energy for these levels to become occupied and contribute to the PL spectrum.

In summary, we have produced high quality epitaxial layers of InAsN containing up to 1% N grown directly on semi-insulating GaAs substrates by MBE. The addition of N improves the PL emission intensity and reduces the thermal quenching. The analysis of the PL spectra of the sample containing 1% N revealed evidence of electron recombination from extended and localized states within the conduction band. The PL emission intensity from all N-containing samples was found to be larger than that from InAs, a result of relevance for the future development of midinfrared optoelectronic devices based on InAsN.

The authors are grateful to the Engineering and Physical Science Research Council (EPSRC) (EP/P503825/1) for providing a studentship for M.d.M. The authors also wish to thank Dr. R. Jones for performing the electron microscope measurements on the samples.

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