

Photoluminescence characterization of midinfrared $\text{InN}_x\text{As}_{1-x}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ multiquantum wells with various N contents

H. D. Sun,^{a)} A. H. Clark, S. Calvez, and M. D. Dawson

Institute of Photonics, University of Strathclyde, 106 Rottenrow, Glasgow, G4 0NW, United Kingdom

D. K. Shih and H. H. Lin

Department of Electrical Engineering, National Taiwan University, Taipei 106, Taiwan, Republic of China

(Received 12 January 2005; accepted 6 July 2005; published online 19 August 2005)

We report the temperature-dependent photoluminescence characterization of $\text{InN}_x\text{As}_{1-x}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ multiple quantum wells with various N contents emitting in the midinfrared wavelength range. The emission wavelength in this material system can be tuned by the N content, but the bowing effect is much weaker than in GaNAs. The correlation between the optical properties and the interface quality is demonstrated by examining the barrier-related emission. The role played by N is elucidated by comparing quantum well samples having either zero, low (0.25%) or high (5%) N content. © 2005 American Institute of Physics. [DOI: 10.1063/1.2034119]

Dilute nitride III-V compound semiconductors have received much attention in recent years due to the intriguing physics arising from the incorporation of small concentrations of nitrogen.¹⁻³ The large band-bowing effect induced by N also gives rise to attractive prospects for optoelectronic devices, of which those in the wavelength range from 1.3 to 1.6 μm based on GaInNAs/GaAs heterostructures have received the majority of attention to date.⁴⁻⁸ On the other hand, there is increasing demand for mid-infrared lasers in the wavelength range from 2 to 5 μm , for applications such as molecular spectroscopy, medical diagnostics, environmental monitoring, free space communication, etc.⁹ Heterostructures based on InNAs dilute nitrides have recently^{10,11} begun to be considered as promising alternatives to more conventional compound semiconductors for this wavelength range. However, until now there have been very few published studies on either InNAs bulk materials or InNAs/InGaAs(P)/InP single quantum wells.¹¹⁻¹³ In this letter we report the photoluminescence characterization of a series of InNAs/InGaAs multiquantum wells (MQWs) of various N content on InP substrates. Emphasis is paid to the correlation of the optical properties to the interface quality. The role of N is elucidated by comparing samples having either low (0.25%) or high (5%) N concentration to samples without N in the QWs.

The MQW samples used in this study consist of 10-period compressively-strained $\text{In}_{1-x}\text{N}_x\text{As}$ (3 nm) QWs and lattice-matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ (40 nm) barriers grown by gas-source molecular beam epitaxy on InP (001) substrates. Elemental In, Ga, and thermally cracked AsH_3 sources were used for In, Ga and As, respectively. The N was generated by a rf plasma source operating at a radio frequency of 13.56 MHz. The InNAs QW was grown at 400 °C, without growth interruption. Due to the simple ternary composition in the QWs, the N content is readily adjusted by the N flow rate. The as-grown composition of N was determined by dynamical simulation of high resolution x-ray diffraction spectra. The sample structures were analyzed by x-ray diffraction and transmission electron microscopy. In this study, we com-

pare a series of samples which are nominally identical in structure but differ only in N content in the range 0–5%. The photoluminescence (PL) measurements were carried out in a liquid He cooled flow cryostat of which the temperature can be controlled from 5 to 300 K. The excitation for the PL measurements was provided by a high power cw diode laser (670 nm). The PL signal was collected in a backscattering geometry via CaF_2 optics, dispersed by a 0.46-m grating monochromator, and then detected by a thermoelectrically cooled InGaAs detector using standard lock-in techniques.

Figure 1 shows the PL spectra at low (5 K) and room (300 K) temperatures, respectively, of three samples of differing N contents (N=0, N=0.25%, and N=5%). All the PL spectra are dominated by an emission band (denoted as band A) with wavelength longer than 2 μm which is attributed to the near-band-edge transition of the QWs. The N-induced bowing effect in these structures is evidenced by the PL red-shift with the increase of the N content. By observing the

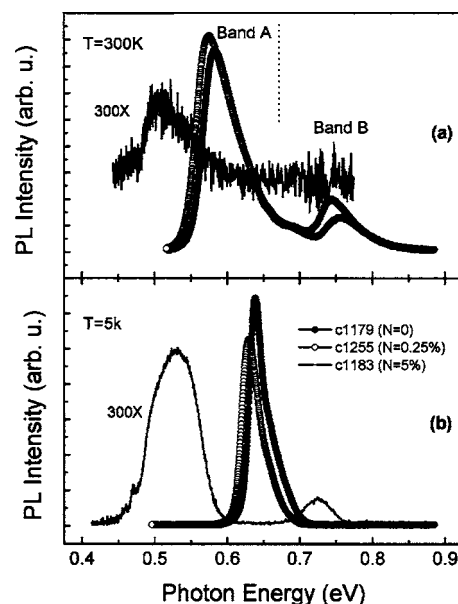


FIG. 1. PL spectra of $\text{InN}_x/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ MQWs with different N contents at (a) 300 K and (b) 5 K.

^{a)} Author to whom correspondence should be addressed; electronic mail: handong.sun@strath.ac.uk

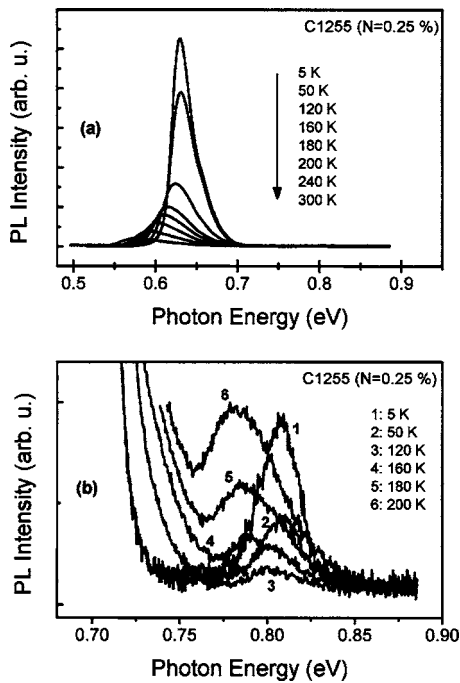


FIG. 2. Temperature dependence of PL spectra of an $\text{InN}_x\text{As}_{1-x}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ ($x=0.25\%$) MQW sample for (a) band A and (b) band B.

room temperature PL for the samples of differing N concentration, it is found that the transition energy reduction rate is about -31 meV/at % N. This is consistent with bulk InNAs material (-36 meV/at % N),¹¹ but much smaller than that for GaNAs (~ -133 meV/at % N).¹⁴ The large bowing effect in dilute nitrides is considered to arise from the interaction between localized N states and the extended states in the matrix.¹⁵ Our observation indicates that the interaction between localized N states and the InAs matrix is much weaker than in GaAs. This result is in agreement with the observation in $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ where the interaction between localized N states and the $\text{Ga}_{1-x}\text{In}_x\text{As}$ matrix decreases as the In mole fraction x increases.¹⁶ Furthermore, it has been found both theoretically and experimentally that the band gap in GaInNAs alloys is related to the atomic bond configuration of N: the band gap is bigger in a N-In rich configuration than it is in a N-Ga rich one.^{17,18} Therefore the lower bowing effect in InNAs should be considered as an intrinsic property of this material system.

Another phenomenon is that, besides the QW-related emission, there exists another emission band at short wavelength (denoted as band B). It is noted that band B is largely suppressed at 5 K for the samples with no, or minimal, N content. In this case, as the dynamic range of the lock-in detection technique is limited, it is barely observable due to the weak intensity relative to the QW emission. However, it can be clearly observed by using a finer measurement scale as shown in Fig. 2. By comparison, in the sample with 5% N concentration, band B is apparent at 5 K but vanishes at 300 K. In order to clarify the origin of band B, temperature-dependent PL spectra have been measured for all these samples. Figure 2 illustrates the PL spectra of both bands at different temperatures for a sample with N content of 0.25% (c1255). The integrated intensity as a function of temperature has been shown in Fig. 3. It is interesting to note that while the PL intensity of band A decreases as temperature in-

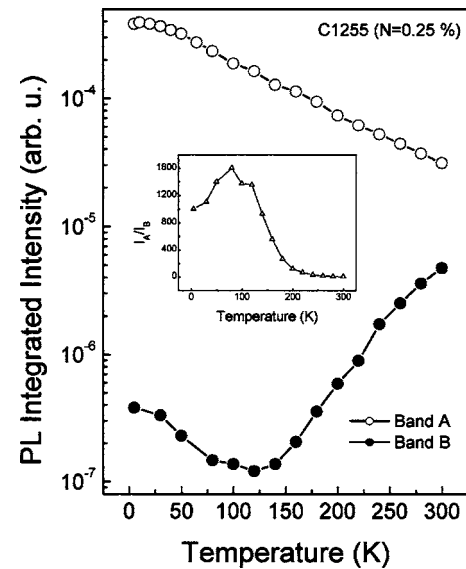


FIG. 3. Integrated PL intensity as a function of temperature for an $\text{InN}_x\text{As}_{1-x}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ ($x=0.25\%$) MQW sample. The inset shows the temperature dependence of the intensity ratio of band A to band B.

creases, the intensity of band B exhibits abnormal behavior: it first decreases from 5 to 120 K and then increases with increasing temperature. The intensity ratio of these two bands as a function of temperature is shown in the inset of Fig. 3, which is very similar to the features of multi-peak emission in GaAs/AlGaAs QW's with growth interruption.¹⁹ In that case, the higher-energy band originates from excitons localized at the heterointerfaces. In our samples, as the energy of band B is very close to the band gap of the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ barriers, we attribute this band to the emission associated with interface, or defect-related, states in the barriers. The abnormal trend of band B actually reflects the competition of carrier capture, carrier relaxation and thermalization.¹⁹ At the lowest temperature, photogenerated carriers can be partially captured by defect-related states at the interfaces and give rise to emission of band B while most of the carriers relax into the QW to give band A. With the increase of temperature, some of the carriers trapped in the interface states may escape by thermalization and relax into the QW. Although carriers in the QWs may also thermalize to the states responsible for band B, the probability is much smaller due to the difference in the energy barriers needing to be overcome. Therefore the PL intensity of band B will decrease rapidly with increasing temperature. However, as the temperature further increases, the carrier transfer process is dominated by thermalization from the QW to the interface and therefore the emission intensity of band B increases.

It should be pointed out that the sample without N in the QWs (c1179) demonstrates similar features to c1255 (N = 0.25%). This implies that one of the reasons for the generation of interface defect states responsible for band B may be the large lattice mismatch between the QWs and the barriers ($\sim 3.2\%$). It is interesting to note that the PL intensity of band A at 5 K of c1179 (N content=0) is stronger than that of c1255 (N=0.25%), but at 300 K the PL intensity of c1255 is apparently stronger than c1179. This indicates that incorporation of small amount N into InAs has decreased the PL quenching rate. A plausible reason is that introduction of N into the InAs QWs decreases the compressive strain in the QWs and therefore the defect density has been reduced. The

reduced strain at the interfaces also contributes to the decreased defect density in the barriers represented by the lower intensity of band B in c1255 than in c1179. It is noted that the emission energy of band B in c1255 is a little bit higher than in c1179. This weaker localization at the interface can also be attributed to the reduced strain in the sample with small amount of N. However, for the sample with 5% N content (c1183), the PL intensity of QW emission is dramatically decreased at both low and high temperatures. This can be attributed to the increase in nonradiative recombination centres due to the increased N content as commonly observed in GaInNAs materials. In this case, the rapid increase in nonradiative recombination centers overbalances the benefit from the reduced strain at the interfaces.

The increased N content in the QWs also influences the behavior of band B. It is observed that at 5 K the *relative* intensity of band B to band A is much larger in samples c1179 and c1255. Meanwhile, the emission energy of band B in c1183 is about 100 meV lower than that of c1179 and c1255. This means that the localization at the interfaces has been deepened by the high N content. This effect may result from the nonuniform distribution of N composition when the average concentration is high. The nonuniformly distributed N atoms at the interfaces interact with the InGaAs barriers, and deep potentials that trap the carriers at low temperature are formed at the interfaces. With the increase of temperature, carriers trapped in these potentials may escape and relax into the QWs, but the thermalized carriers from the QWs have little chance to be recaptured by the interface potential because they are first depleted by nonradiative recombination. That is why the intensity of band B in sample c1183 decreases monotonically with increasing temperature. It is worthwhile to note that this behavior is different from those in samples c1179 and c1255 and the situation described in Ref. 19 where the thermal migrations between two regions dominated the nonradiative processes, rather than nonradiative recombination.

The above analysis indicates that the behaviour of band B provides information about the interfaces which is correlated to the photoluminescence from the QWs. As the optical quality of InNAs QWs is sensitive to the strain at the interfaces and the N concentration, it should be advantageous for the lattice-matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ barriers to be replaced by strain-compensating and/or strain-mediating layers as in GaInNAs/GaAs materials.^{20–22} This can be realized by adjusting the composition of $\text{Ga}_{(1-x)}\text{In}_x\text{As}$. Considering the 0.36 eV band gap of InAs, the band-gaps of our QW samples are in effect too large due to the quantum confinement energy induced by the narrow width (3 nm) of the QWs (imposed by the big lattice-mismatch between the barriers and QWs). The introduction of strain-compensating and/or strain-mediating layers will definitely increase the effective width of the QWs and therefore extend the emission to longer wavelength.

In conclusion, the optical properties of GSMBE-grown midinfrared InNAs/InGaAs/InP MQW samples of differing N contents have been investigated at various temperatures. The emission wavelength of these QWs can be controlled effectively by the N content, however the band-bowing effect is weaker than in GaNAs and GaInNAs. The optical properties in these heterostructures are closely related to the quality of interfaces between the barriers and the QWs, which is influenced by N content. Two effects of N in this material system have been clarified. On the one hand, the incorporation of N into an InAs matrix is beneficial as far as the reduction of band gap and the lattice constant are concerned. On the other hand, the PL efficiency decreases dramatically with the increase of N content. Employing strain-compensating and/or strain-mediating layers is proposed to improve the QW structure regarding the emission efficiency and wavelength.

¹M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, *Jpn. J. Appl. Phys., Part 1* **35**(2B), 1273 (1996).

²I. A. Buyanova, W. M. Chen, and B. Monemar, *MRS Internet J. Nitride Semicond. Res.* **6**, 2 (2001).

³P. J. Klar, H. Gruning, W. Heimbrodt, J. Koch, W. Stolz, S. Tomic, and E. P. O'Reilly, *Surf. Sci. Spectra* **47**, 437 (2003).

⁴T. Kitatani, M. Kondow, S. Nakatsuka, Y. Yazawa, and M. Okai, *IEEE J. Sel. Top. Quantum Electron.* **3**, 206 (1997).

⁵S. R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, J. J. Banas, and B. E. Hammons, *Appl. Phys. Lett.* **74**, 729 (1999).

⁶M. C. Larson, M. Kondow, T. Kitatani, K. Nakahara, K. Tamura, H. Inoue, and K. Uomi, *IEEE Photonics Technol. Lett.* **10**, 188 (1998).

⁷H. Riechert, A. Ramakrishnan, and G. Steinle, *Semicond. Sci. Technol.* **17**, 892 (2002).

⁸H. D. Sun, G. J. Valentine, R. Macaluso, S. Calvez, D. Burns, M. D. Dawson, T. Jouhti, and M. Pessa, *Opt. Lett.* **27**, 2124 (2002); A. H. Clark, G. J. Valentine, R. Macaluso, S. Calvez, D. Burns, M. D. Dawson, T. Jouhti, and M. Pessa, *IEEE J. Quantum Electron.* **40**, 878 (2004); J. M. Hopkins, S. A. Smith, C. W. Jeon, H. D. Sun, D. Burns, S. Calvez, M. D. Dawson, T. Jouhti, and M. Pessa, *Electron. Lett.* **40**, 30 (2004).

⁹J. Wagner, C. H. Mann, M. Rattunde, and G. Weimann, *Appl. Phys. A: Mater. Sci. Process.* **78**, 505 (2004).

¹⁰D. K. Shih, H. H. Lin, and Y. H. Lin, *Electron. Lett.* **37**, 1342 (2001).

¹¹H. Naoi, Y. Naoi, and S. Sakai, *Surf. Sci. Spectra* **41**, 319 (1997).

¹²J. C. Fan, W. K. Hung, Y. F. Chen, J. S. Wang, and H. H. Lin, *Phys. Rev. B* **62**, 10990 (2000).

¹³G. R. Chen, H. H. Lin, J. S. Wang, and D. K. Shih, *J. Appl. Phys.* **90**, 6320 (2002).

¹⁴S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishin, and H. Temkin, *Appl. Phys. Lett.* **72**, 1857 (1998).

¹⁵W. Shan, W. Walukiewicz, and J. W. Ager III, *Phys. Rev. Lett.* **82**, 1221 (1999).

¹⁶M. Hetterich, A. Grau, A. Y. Egorov, and H. Riechert, *J. Appl. Phys.* **94**, 1810 (2003).

¹⁷K. Kim and A. Zunger, *Phys. Rev. Lett.* **86**, 2609 (2001).

¹⁸V. Lordi, V. Gambin, S. Friedrich, T. Funk, T. Takizawa, K. Uno, and J. S. Harris, *Phys. Rev. Lett.* **90**, 145505 (2003).

¹⁹Z. L. Yuan, Z. Y. Xu, B. Z. Zheng, C. P. Luo, J. Z. Xu, W. K. Ge, P. H. Zhang, and X. P. Yang, *J. Appl. Phys.* **79**, 1073 (1996).

²⁰E. M. Pavele, C. S. Peng, T. Jouhti, J. Kontinen, W. Li, M. Pessa, M. Dumitrescu, and S. Spănulescu, *Appl. Phys. Lett.* **80**, 3054 (2002).

²¹H. D. Sun, A. H. Clark, H. Y. Liu, M. Hopkinson, S. Calvez, M. D. Dawson, Y. N. Qiu, and J. M. Rorison, *Appl. Phys. Lett.* **85**, 4013 (2004).

²²H. D. Sun, A. H. Clark, S. Calvez, M. D. Dawson, K. S. Kim, T. Kim, and Y. J. Park, *Appl. Phys. Lett.* **87**, 021903 (2005).