

Molecular beam epitaxial growth of InAsN:Sb for midinfrared Optoelectronics

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We report molecular beam epitaxial growth and characterization of dilute nitride InAsN:Sb. X-ray diffraction, energy dispersive x-ray spectrometry, and electron probe microanalysis revealed that nitrogen incorporation is significantly enhanced by introduction of Sb flux during growth, together with a dramatic improvement of the photoluminescence. These observations were attributed to the surfactant effect of Sb which suppresses the surface diffusion length of nitrogen and improves the homogeneity of the alloy. Sb incorporation is enhanced with the presence of nitrogen which was associated with the surface kinetic of growth. InAsN:Sb/InAs *p-i-n* light emitting diodes operating near 4.0 μm were also realized. © 2008 American Institute of Physics. [DOI: 10.1063/1.2988281]

Dilute nitride alloys containing a small amount of nitrogen are particularly of interest due to the large bandgap reduction,¹ unique physics,² and a wide variety of device applications in near-infrared spectral range.^{3,4} Recently, incorporation of nitrogen into narrow bandgap materials has attracted increasing attention due to the capability to enable emission in midinfrared (MIR) spectral range⁵ and the suppressed Auger recombination.⁶ Although InAsN/InGaAs quantum well lasers operating at 2.38 μm have been demonstrated,⁷ no MIR light emitters have yet been realized due to the difficulty in growing device quality InAsN.^{8,9} Weak, broad photoluminescence (PL) emission from InAsN has been reported¹⁰ with observation of strong localized states which have been theoretically interpreted.¹¹ Recently, we produced device quality InAsN and reported bright PL emission near 4.5 μm at room temperature.¹² In this letter, we report the further improvement of InAsN by addition of Sb during growth. We observed that introduction of Sb flux dramatically enhances nitrogen incorporation and significantly improves optical properties. In addition, Sb incorporation is enhanced with the presence of nitrogen. We also report the realization of InAsN:Sb/InAs MIR light emitting diodes (LEDs) operating at 4.0 μm .

The samples of 1- μm -thick InAsN:Sb epilayers were grown on InAs substrates by molecular beam epitaxy (MBE) using a radio frequency plasma nitrogen source, at growth temperature of 420 °C, growth rate of 1.0 $\mu\text{m}/\text{h}$, and As flux of 2.2×10^{-6} mbar. The nitrogen plasma setting was fixed at a power of 160 W and a nitrogen flux of 5.0×10^{-7} mbar. A valved cracker cell was used to vary Sb flux. 1- μm -thick epilayers of InAsN and InAsSb were grown using the above conditions as reference samples.

High resolution double crystal x-ray diffraction (DCXRD), energy dispersive x-ray spectrometry (EDX) and electron probe microanalysis (EPMA) were employed to determine N and Sb compositions. PL measurements were carried out to investigate the optical properties with an Ar⁺ ion laser (514 nm) which produced an excitation power density up to 20 W cm⁻², in the temperature range of 4–300 K.

Figure 1 shows the DCXRD rocking curves from the epilayers. Reference samples of InAsN and InAsSb exhibit tensile and compressive strain, respectively, and 0.7% of N and 4.8% Sb were deduced. For InAsN:Sb epilayers, introduction of Sb during growth clearly shifts the epilayer peak relative to the substrate, indicating reduction in the strain. This reveals the possibility to grow lattice-matched InAsN:Sb on InAs for practical devices. The full width at half maximum of InAsN:Sb epilayers is narrower than that of InAsN epilayers at similar strain. This demonstrates the improved crystalline quality of the material obtained by introduction of Sb, which was further confirmed by PL measurements.

In order to determine the composition of N and Sb in the InAsN:Sb alloy, EDX and EPMA were used to obtain the Sb composition (these two techniques are not accurate enough to give N composition at very low levels), and the N composition was deduced from the DCXRD measurements assuming that the samples obey Vegard's law. The composition dependence of N and Sb upon Sb/As ratio is presented in

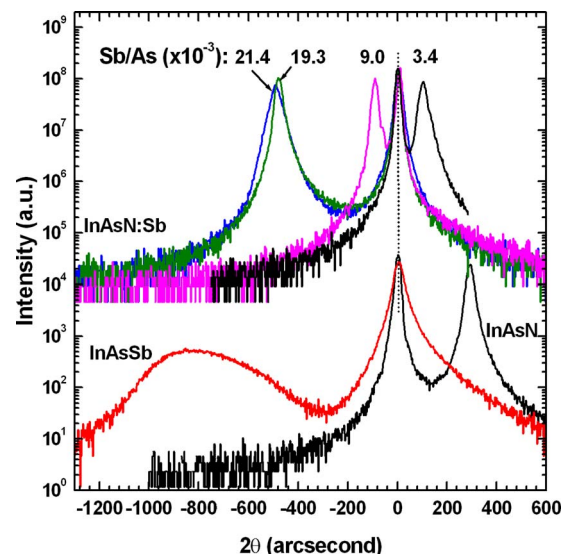


FIG. 1. (Color online) DCXRD rocking curves from a series of InAsN:Sb epilayers grown at different Sb fluxes.

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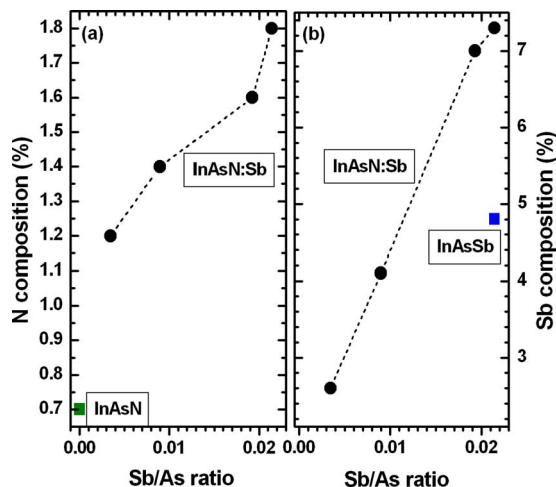


FIG. 2. (Color online) Dependence of N composition on Sb/As ratio (a) and dependence of Sb composition on Sb/As ratio (b) in InAsN:Sb alloy.

Fig. 2 together with reference samples of InAsN and InAsSb. Clearly, the introduction of Sb enhances nitrogen incorporation, and this enhancement increases with increase in the Sb flux. 1.8% N composition was obtained in InAsN:Sb at Sb flux of 4.5×10^{-8} mbar, which is ~ 2.5 times to that in the InAsN reference sample. In addition, Sb incorporation is enhanced (by ~ 1.5 times) in the presence of nitrogen compared with InAsSb. This N (Sb) incorporation enhancement due to the presence of Sb (N) can be understood from the surface growth kinetics.

Sb was initially introduced to improve the optical quality of GaAs-based GaInAsN material as a surfactant and lasers with lower threshold current density and improved slope efficiency were realized.¹³ It was also examined as an effective means to extend the operating wavelength,^{14–16} which was attributed to the incorporation of Sb and the enhanced N incorporation.¹⁷ Lasers operating at wavelength $\geq 1.55 \mu\text{m}$ with better performance compared to GaInAsN lasers have been realized.^{18–20} Although this enhanced N incorporation obtained by adding Sb was assumed to be associated with the increased nitrogen sticking coefficient,^{14–17,21} the cause for such an increase in sticking coefficient remains unclear.¹⁴ We believe that the surface growth kinetics are mainly responsible. It is generally accepted that Sb acts as a surfactant which reduces the surface diffusion length.²² In MBE growth of GaAsN and InAsN, nitrogen incorporation is strongly dependent on the growth temperature and growth rate.^{12,23} A model involving nitrogen surface diffusion interpreted this behavior and indicates that nitrogen diffusion plays a crucial role during growth. When Sb is introduced, the nitrogen surface diffusion length is reduced due to the strong Sb surfactant effect, and consequently leads to an enhanced N incorporation. With an increase in Sb flux, the coverage of Sb on the growth surface is larger which causes a stronger surfactant effect and results in more nitrogen incorporation.

The increase in Sb incorporation in the presence of nitrogen has not been previously reported, although incorporation of Sb was revealed in GaInAsN grown using assistant Sb.^{15,16,21} Due to the strong Sb segregation during growth,²⁴ such an increase can be attributed to the reduction of Sb segregation induced by nitrogen. The segregation of atoms on semiconductor surfaces is determined by atom kinetic mobility close to the surface (related to the activation energy

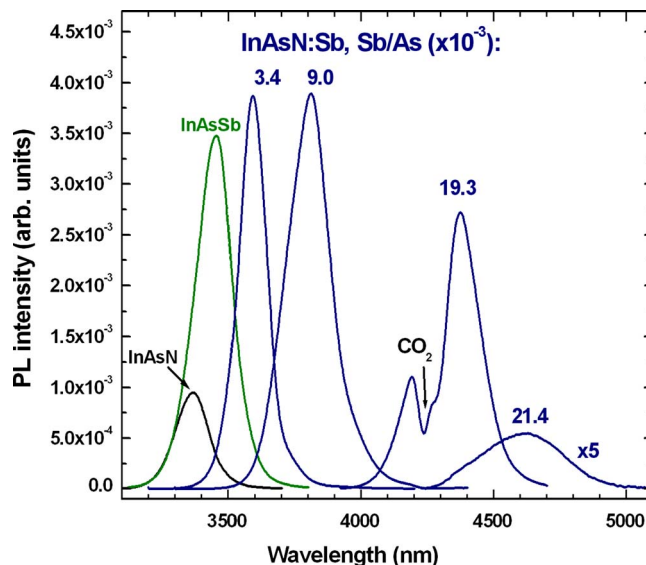


FIG. 3. (Color online) PL spectra at 4 K from InAsN:Sb epilayers and reference samples of InAsN and InAsSb.

for diffusion E_{diff}) and the thermodynamic driving force for segregation (related to the enthalpy of segregation E_{seg}).²² At low growth temperatures, segregation is kinetically limited and dominated by the E_{diff} term which is in agreement with our experimental results, showing an increase in segregation as the temperature increases (Sb composition decreases at higher growth temperature). It was reported that the E_{diff} term has a strong dependence on compressive biaxial stress in the epilayer, and in the Sb doping of SiGe, enhanced Sb segregation with increase of Ge was observed.²⁵ In our experiments, the presence of nitrogen in the InAsSb epilayer on InAs reduces the compressive strain, which leads to a reduced Sb segregation, and results in an enhanced Sb incorporation. Furthermore, segregation enthalpy (E_{seg}) can play a significant role at low temperature due to three main parameters:²² (i) the difference in surface energy between solute (Sb) and solvent (InAsN), (ii) the difference in atom size, and (iii) the tendency toward phase separation (mixing energy). In our experiments, we observe that (i) N has a higher surface free energy than As,¹³ its addition will increase the alloy surface energy and thus decrease the tendency for Sb to segregate, (ii) N has a smaller atomic size, its addition decreases lattice parameter and thus increases the steric effect, and (iii) no significant phase separation was observed for InSbN and InAsN at low nitrogen level ($< 3\%$ in our experiments) at low growth temperature. Combination of these three effects results in a further reduction of Sb segregation. Consequently Sb incorporation is enhanced in the presence of nitrogen.

Figure 3 shows the 4 K PL from our InAsN:Sb epilayers. The peak intensity from InAsN is weaker than InAsSb by a factor of ~ 4 indicating the severe degradation due to nitrogen incorporation. With the introduction of Sb, significantly brighter emission is evident which is comparable to the intensity of InAsSb (without correction of spectral response of detector and grating for the emission near $4.6 \mu\text{m}$). This indicates that the introduction of Sb dramatically improves the optical properties of InAsN. Our results are in good agreement with previous observations on InGaAsN:Sb which was associated with Sb surfactant effects.^{13,16} The sur-

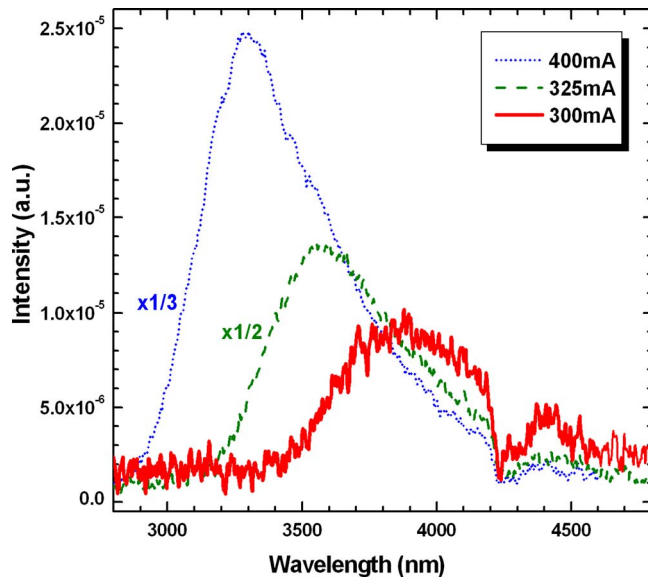


FIG. 4. (Color online) EL spectra from InAsN:Sb/InAs *p-i-n* LEDs at 4 K using different drive currents.

factant effect improves crystalline quality and homogeneity of the alloy and is consistent with the DCXRD measurements. This improvement suppresses the well-known localized states in dilute nitrides and symmetric spectra are evident (the double-peak feature of the emission near $4.3 \mu\text{m}$ is due to absorption of CO_2 in the laboratory atmosphere) so that the PL emission from InAsN:Sb epilayers is associated with direct band-band recombination, which is similar to our previously reported findings for InAsN.²⁶ In addition, strong PL emission is evident at room temperature in InAsN:Sb epilayers with a redshift of $\sim 24 \text{ meV}$.

The above results are promising for device applications of InAsN:Sb in MIR optoelectronics. Consequently, a lattice-matched/InAs *p-i-n* sample containing a $1\text{-}\mu\text{m}$ -thick InAsN:Sb sandwiched between $0.5\text{-}\mu\text{m}$ -thick *p*-InAs and *n*-InAs contact layers was subsequently fabricated into 1 mm diameter mesa-etched LEDs. Electroluminescence (EL) under quasicontinuous drive conditions (1 kHz at 50% duty cycle) was measured at 4 K using a Bentham 0.3 m monochromator and a 77 K InSb photodiode. EL spectra using different drive currents are shown in Fig. 4, where emission near $4.0 \mu\text{m}$ was obtained using the lowest injection current. With an increase in drive current, the EL emission shows a significant blueshift of the peak energy and an asymmetric spectrum with a long wavelength tail. These behaviors can be attributed to the band-filling effect. An increase in carrier concentration in semiconductor results in two opposite effects on the recombination energy: a decrease due to the exchange interaction and an increase due to the band filling. It was reported that the band filling is predominant at high carrier concentration which is proportional to the term of $n^{2/3}$, where n is the carrier concentration.²⁷ This band-filling effect is assumed to be the cause of the asymmetric spectral EL emission.

In summary, InAsN:Sb epilayers on InAs substrate were grown by MBE using various Sb fluxes. Sb plays a beneficial

role as a surfactant during the growth, resulting in a significantly enhanced nitrogen incorporation and substantial improvement of the optical properties. Meanwhile, the presence of nitrogen enhances the Sb incorporation as well. These effects led to the realization of lattice-matched InAsN:Sb *p-i-n* LEDs operating near $4.0 \mu\text{m}$. Our investigation of this narrow bandgap alloy demonstrates the potential applications for MIR optoelectronics.

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- ¹M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, *Jpn. J. Appl. Phys., Part 2* **33**, L1056 (1994).
- ²W. Shan, W. Walukiewicz, J. W. Ager, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.* **82**, 1221 (1998).
- ³N. Balkan, in *The Physics and Technology of Dilute Nitrides*, special issue of *J. Phys. Condens. Matter* **16**, 31 (2004).
- ⁴*Dilute Nitride Semiconductors*, edited by M. Henini (Elsevier, Amsterdam, 2005), pp. 1–92 and references therein.
- ⁵M. Osinski, *Opto-Electron. Rev.* **11**, 321 (2003).
- ⁶B. N. Murdin, M. Kamal-Saadi, A. Lindsay, E. P. O'Reilly, A. R. Adams, G. J. Nott, J. G. Crowder, C. R. Pidgeon, I. V. Bradley, J. P. R. Wells, T. Burke, A. D. Johnson, and T. Ashley, *Appl. Phys. Lett.* **78**, 1568 (2001).
- ⁷D. K. Shih, H. H. Lin, and Y. H. Lin, *Electron. Lett.* **37**, 1342 (2001).
- ⁸R. Beresford, K. S. Stevens, and A. F. Schwartzman, *J. Vac. Sci. Technol. B* **16**, 1293 (1998).
- ⁹J. Wagner, K. Kohler, P. Ganser, and M. Maier, *Appl. Phys. Lett.* **87**, 051913 (2005).
- ¹⁰T. D. Veal, L. F. J. Piper, P. H. Jefferson, I. Mahboob, C. F. McConville, M. Merrick, T. J. C. Hosea, B. N. Murdin, and M. Hopkinson, *Appl. Phys. Lett.* **87**, 182114 (2005).
- ¹¹M. Merrick, S. A. Cripps, B. N. Murdin, T. J. C. Hosea, T. D. Veal, and C. F. McConville, M. Hopkinson, *Phys. Rev. B* **76**, 075209 (2007).
- ¹²Q. Zhuang, A. M. R. Godenir, A. Krier, K. T. Lai, and S. K. Haywood, *J. Appl. Phys.* **103**, 063520 (2008).
- ¹³X. Yang, M. J. Jurkovic, J. B. Heroux, and W. I. Wang, *Appl. Phys. Lett.* **75**, 178 (1999).
- ¹⁴J. C. Harmand, G. Ungaro, L. Largeau, and G. Le Roux, *Appl. Phys. Lett.* **77**, 2482 (2000).
- ¹⁵L. H. Li, V. Sallet, G. Patriarche, L. Largeau, S. Bouchoule, L. Travers, and J. C. Harmand, *Appl. Phys. Lett.* **83**, 1298 (2003).
- ¹⁶S. R. Bank, H. B. Yuen, H. Bae, M. A. Wistey, A. Moto, and J. S. Harris, *Appl. Phys. Lett.* **88**, 241923 (2006).
- ¹⁷H. D. Sun, S. Calvez, M. D. Dawson, J. A. Gupta, G. I. Sproule, X. Xu, and Z. R. Walsilewski, *Appl. Phys. Lett.* **87**, 181908 (2005).
- ¹⁸X. Yang, J. B. Heroux, L. F. Mei, and W. I. Wang, *Appl. Phys. Lett.* **78**, 4068 (2001).
- ¹⁹Z. C. Niu, S. Y. Zhang, H. Q. Ni, D. H. Wu, H. Zhao, H. L. Peng, Y. Q. Xu, S. Y. Li, Z. H. He, Z. W. Ren, Q. Han, X. H. Yang, Y. Du, and R. H. Wu, *Appl. Phys. Lett.* **87**, 231121 (2005).
- ²⁰J. A. Gupta, P. J. Barrios, J. A. Caballero, D. Poitras, G. C. Aers, G. Pakulski, and X. Wu, *Appl. Phys. Lett.* **89**, 151119 (2006).
- ²¹K. Volz, V. Gambin, W. Ha, M. A. Wistey, H. Yuen, S. Bank, and J. S. Harris, *J. Cryst. Growth* **251**, 360 (2003).
- ²²A. Portavoce, I. Berbezier, P. Gas, and A. Ronda, *Phys. Rev. B* **69**, 155414 (2004).
- ²³Z. Pan, L. H. Li, W. Zhang, Y. W. Lin, and R. H. Wu, *Appl. Phys. Lett.* **77**, 214 (2000).
- ²⁴J. F. Nuzel and G. Abstreiter, *Phys. Rev. B* **53**, 13551 (1996).
- ²⁵P. Kringhoj, A. Nylandsted Larsen, and S. Yu. Shirayev, *Phys. Rev. Lett.* **76**, 3372 (1996).
- ²⁶Q. Zhuang, A. Godenir, and A. Krier, *J. Phys. D* **41**, 132002 (2008).
- ²⁷I. T. Yoon, T. S. Ji, S. J. Oh, J. C. Choi, and H. L. Park, *J. Appl. Phys.* **82**, 4024 (1997).