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Properties of dilute InAsN layers grown by liquid phase epitaxy

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We report on the liquid phase epitaxial growth of InAsN from indium rich solution. The spectral properties of dilute bulk alloys containing N ~ 0.5% and which exhibit photoluminescence in the midinfrared spectral range without any postgrowth annealing are described. The blueshift in the emission spectrum is attributed to a combination of tensile strain and band filling effects. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2975166]

The narrow gap III-V dilute nitride compound InAsN is of special interest due to its potential applications for use in optoelectronic devices operating in the midinfrared spectral region which is rich in applications.[1–3] The addition of small quantities of nitrogen to III-V semiconductors has generally been found to result in a large band gap bowing[4] and a significant reduction in the band gap of the material.[5] In the case of InAsN this property could be used to reduce the band gap further from that of InAs thereby making the material an alternative to other midinfrared materials, such as HgCdTe, PbSnTe, and InAsSb. The advantage of using InAsN is the ability to tune the band gap down to a very low value by controlling the amount of nitrogen incorporated and, in principle, to grow the alloy nearly lattice matched not only to InAs[6] but also to GaAs[7] and InP[8] by using appropriate amounts of nitrogen. InAsN single layers and quantum wells have so far been grown by molecular beam epitaxy[6–9] (MBE) and metal-organic vapor phase epitaxy.[3,10,11] Liquid phase epitaxy (LPE), which is a thermal equilibrium growth technique, capable of producing epitaxial materials with excellent crystalline perfection and high luminescence efficiency, can avoid some of the problems associated with ion damage from the N plasma used in MBE growth of dilute nitrides and so is an attractive alternative. However, it has only very recently been used for the growth of high quality GaAsN[12–14] and GaSbN[15] using polycrystalline GaN as the source of nitrogen in the growth melt. In this paper we report on the LPE growth of InAsN and the photoluminescence (PL) emission properties of the resulting epitaxial layers.

LPE growth of the InAsN layers was done in a horizontal tube reactor using a transparent gold furnace and high purity quartz tube. The growth boat was made of high purity, high density graphite obtained from *Poco Graphite*, USA. Prior to growth, the reactor together with the graphite boat, were baked for several hours at high temperature under Pd-diffused ultrapure hydrogen gas. Initially, 99.999 99% pure In metal, procured from *JMC Ltd.*, USA, was loaded in to the boat and baked at 780 °C for 18–20 h under purified hydrogen flow. The required quantity of 99.9999% polycrystalline (JMC) InAs was then added to the In contained in the growth melt bin and baked again at 750 °C for the same period. Finally, precisely weighed amounts of 99.8% polycrystalline InN, obtained from *Alfa Aesar*, USA, were added to the growth melt and baked at 700 °C for 1–2 h. Growth was typically commenced at 590 °C for 7–8 min using a melt supersaturation of 5–6 °C and a constant cooling rate of 0.3 °C/min onto InAs (100) substrates.

After growth, the surface of the layer was inspected using a Nomarski phase contrast microscope. To detect the presence of N in the grown layers, energy dispersive X-ray analysis (EDX) measurements were done in a *Quanta FEG200* scanning electron microscope. The structural properties of the layers were investigated using high resolution x-ray diffraction (HRXRD) measurements in a Philips X'Pert diffractometer. PL measurements were made on the resulting layers over the range from 4 to 150 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. A computer was used to control the monochromator and record the final signal using LABVIEW operating software.

The EDX spectrum obtained from one of the InAsN LPE-grown layers is presented in Fig. 1. In addition to the two major peaks, from the In and As, a smaller peak is observable at low energy, which is consistent with the presence of N in the sample and which confirms that nitrogen has entered the grown material. The result from an HRXRD scan of one of the layers is shown in Fig. 2. The insets in the

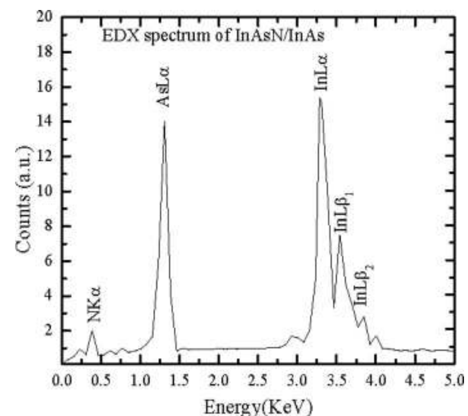

FIG. 1. The energy dispersive x-ray microanalysis spectrum measured from one of the InAsN LPE-grown samples.

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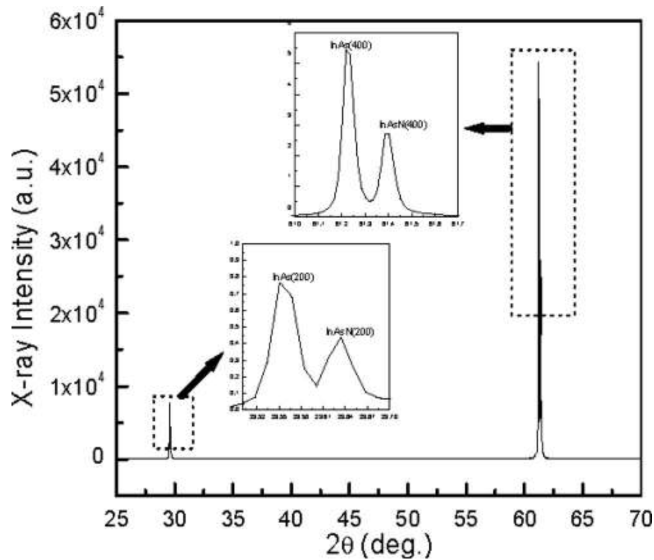

FIG. 2. A HRXRD spectrum obtained from one of the InAsN samples (ISN14). The insets show the details of the (200) and (400) reflections.

figure show expanded forms of the peaks for the (200) and (400) reflections. Two peaks due to InAsN and the substrate InAs are clearly resolved in each case. No peak due to cubic InN or hexagonal InN is found in the spectrum, which confirms that a single crystalline layer of epitaxial InAsN has been formed. The angular separation between the substrate and InAsN peaks gives a measure of the lattice mismatch introduced as a result of nitrogen incorporation and from which the nitrogen content in this particular layer (ISN14) was calculated to be 0.56%, using Vegard's law.[16]

Figure 3 shows the 4 K PL spectra for two InAsN samples containing different amounts of N. Both the spectra have very similar appearance with four peaks, labeled A–D being resolved in each spectrum. These peaks can be readily associated with the characteristic transitions observed in InAs[17,18] and are identified as follows. Peaks A and B originate from band-band transitions and donor-acceptor pairs,

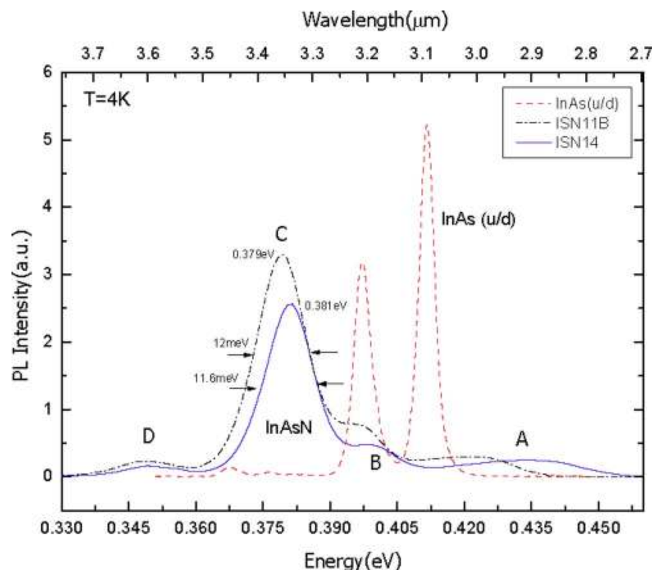

FIG. 3. (Color online) The 4 K PL emission spectra measured from two InAsN samples. ISN14 (0.56%) and ISN 11B (0.50%). The PL spectrum from a high purity LPE-grown InAs layer (dashed line) containing zero N is also presented for comparison.

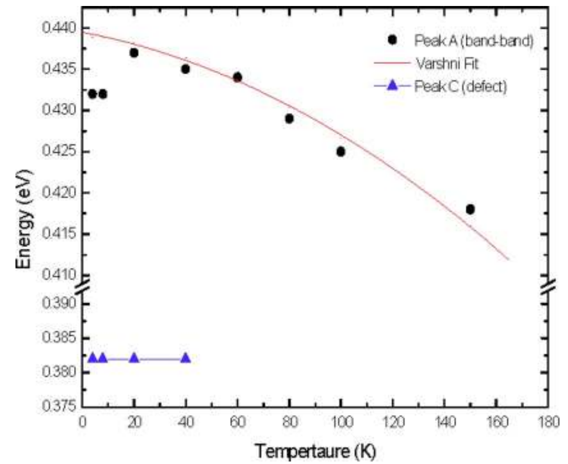

FIG. 4. (Color online) The temperature dependent PL spectra measured from one of the LPE-grown InAsN samples (ISN11B).

respectively, whereas peak C (0.38 eV) is the most prominent in the spectrum and may be attributed to recombination via a defect state.[19,20] However, we note that the peaks are systematically blueshifted to slightly higher energy compared to their generally accepted energies in undoped binary InAs. The PL spectrum of "typical" LPE-grown InAs (containing zero N) is also shown in Fig. 3 for comparison. We attribute the blueshift in our InAsN to a combination of tensile strain and Moss–Burstein band filling effects. The latter may be associated with residual impurities, presumably from the InN precursor in the melt, and which contribute to an increased carrier concentration. We note that this is consistent with previous findings from transmission measurements on InAsN,[9] where increasing N led to an apparent increase in the bandgap associated with band filling originating from residual carriers produced by introducing increasing amounts of N. Although this is most likely the major effect we also consider a contribution from strain. PL spectra from InAs grown on Si substrates have been studied previously and found to exhibit a redshift arising from the residual compressive strain in the epitaxial layer on cooling.[19] In our case the epitaxial InAsN is under tensile strain and although the layer thickness of 2–3 μm is above the critical layer thickness, it is conceivable that not all the strain is relieved by the formation of dislocations, resulting in a blueshift.

As shown in Fig. 4, at low temperatures the peak emission deviates from the usual temperature dependence of the band gap.[23] From the position of peak A, the apparent band gap of the material at 4 K is estimated at 0.430 eV (in ISN14), which increases to 0.437 eV at 20 K and again decreases to 0.418 eV at 150 K. This behavior is associated with localization of carriers and is common in InAsN,[6,21] where at low temperatures, PL emission is dominated by transitions involving states below the band gap consistent with the band anticrossing model.[22] At elevated temperatures, electrons from these states are thermally excited back into the conduction band and the peak emission is primarily due to band-band recombination. Above 75 K the PL peak emission energy follows closely the theoretical dependence with temperature, drawn assuming a nitrogen content of 0.23% in the material using the functional form of fitting to the empirical Varshni equation[23]

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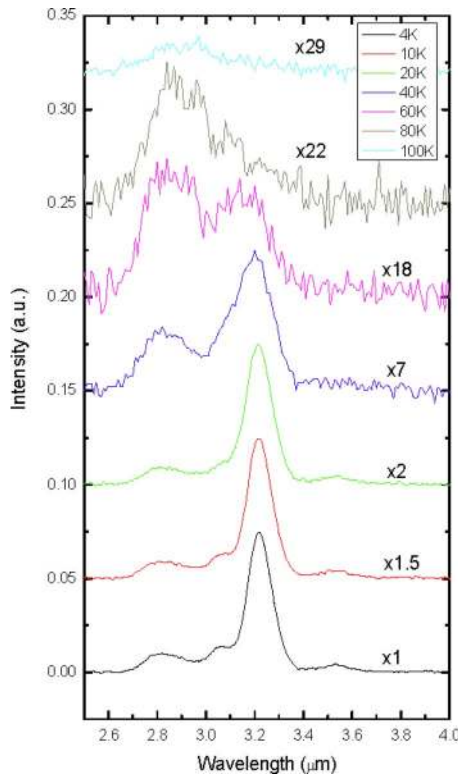

FIG. 5. (Color online) Temperature dependence of the PL emission peaks observed from sample ISN14.

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}. \quad (1)$$

The Varshni parameters are α=0.276 meV/K and β=93 K based on values taken from Ref. 24.

The assignment of the principal peak C as a defect related recombination is justified from the dependence of the PL intensity on temperature, as shown in Fig. 5. At 80 K and above, peak A becomes most prominent whereas peak C reduces and becomes completely quenched at 150 K, while the phonon replica peak D disappears above 80 K. Moreover, as shown in Fig. 5 the peak emission energy of peak C hardly changes with increasing temperature. This behavior is a characteristic of transitions involving a defect state which becomes thermally ionized at elevated temperatures and supports our identification of peak C.

In summary, we have produced bulk epitaxial layers of InAsN containing up to 0.56% N by using liquid phase epitaxial growth and adding InN as a solid source of N to the In melt solution. The resulting as-grown samples exhibited PL consistent with that of a dilute InAsN alloy. The PL emission spectra were dominated by transitions involving a defect at low temperatures. A blueshift in the emission spectra was attributed mainly to band filling effects arising from residual impurities.

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