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Rapid Research Note

Band Gap of InN and In-Rich $In_xGa_{1-x}N$ alloys ($0.36 < x < 1$)

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InN and In-rich alloys have not been investigated thoroughly because of difficulties associated with the growth of these compounds. Recently the improved growth techniques have made it possible to obtain single-crystalline InN layers. Optical measurements on these layers revealed a strong photoluminescence (PL) band near the absorption edge in a range of 0.75 eV to 0.9 eV [1]. In the present work we argue that the PL bands of non-intentionally doped InN samples studied are similar to the high-energy bands in PL spectra of heavily doped III–V or II–VI crystals. Analysis of the PL data leads to the conclusion that the true band gap is much smaller than the value of 1.8 eV reported previously [2]. These findings are strongly supported by PL studies of In-rich $In_xGa_{1-x}N$ alloys.

Single-crystalline n-InN epilayers were grown on sapphire substrates by metalorganic chemical vapor deposition [3] (sample 1) and metalorganic molecular-beam epitaxy [4] (samples 2, 3, 4) techniques. A set of $In_xGa_{1-x}N$ alloys ($0.36 < x < 1$) was grown by plasma-assisted molecular-beam epitaxy under the conditions similar to those for InN [5]. Only a hexagonal structure was established by X-ray and Raman measurements in the InN and $In_xGa_{1-x}N$ alloys. An argon laser (2.54 eV) was used as excitation source in the PL measurements.

The high-energy PL band in heavily doped semiconductors results from the recombination of degenerate electrons with photo-holes near the top of the valence band. Based on the valence–conduction band diagram [6] and results of [7], the shape of the PL band at $\hbar\omega > E_G$ can be described by

$$I(\hbar\omega) \sim [\hbar\omega - E_G]^{\gamma/2} f(\hbar\omega - E_G - E_F)\,, \tag{1}$$

where E_G is a charge carrier concentration-dependent parameter related to the band gap E_g, E_F is the Fermi energy for the degenerate electrons, and $f(\hbar\omega - E_G - E_F) = 1/[\exp\{(\hbar\omega - E_G - E_F)/kT\} + 1]$ is a Fermi distribution function. The value $\gamma = 1$ holds if only vertical interband transitions are allowed, or $\gamma = 4$ is valid if the momentum conservation law is completely broken due to the influence of defects and/or impurities on the hole states. The PL band shape has two characteristic features. The first is a high-energy wing showing an exponential decrease in the region of $(\hbar\omega - E_G) \approx E_F$ due to a decrease in the electron population in accordance with the Fermi func-

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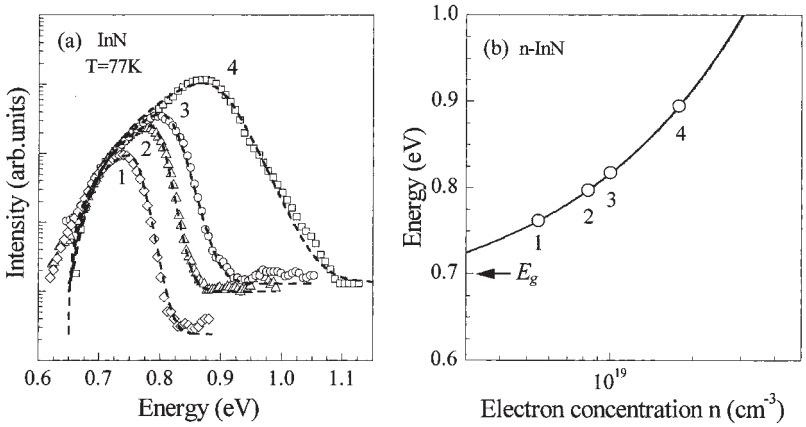

Fig. 1. a) Open symbols, semilog PL spectra of InN layers with different carrier concentrations: $n = 6 \times 10^{18}\,\mathrm{cm}^{-3}$ (1), $n = 9 \times 10^{18}\,\mathrm{cm}^{-3}$ (2), $n = 1.1 \times 10^{19}\,\mathrm{cm}^{-3}$ (3), and $n = 4.2 \times 10^{19}\,\mathrm{cm}^{-3}$ (4). Dashed lines, fitted curves. b) Calculated shift of optical absorption edge due to the Burstein–Moss effect in n-type InN (solid line). Open circles mark $E_G + E_F$ positions estimated from PL spectra in our samples

tion $f(\hbar\omega - E_G - E_F)$. The second is the low-energy wing at $\hbar\omega < E_G$ that typically shows the Urbach tail, which can overlap with transitions related to the recombination of electrons with deeper localized states of holes.

Figure 1a displays PL spectra at 77 K for InN and the fitted curves obtained from Eq. (1). The fit shows that $\gamma = 4$ should be used. The temperature estimated from the exponential slope of the high-energy wing of the PL bands is close to the measured temperature for all crystals except sample 4. This discrepancy is probably due to an inhomogeneous structure of the sample caused by a very high doping level. From Eq. (1) follows that the low-energy parts of the fitted curves tend to zero at $\hbar\omega \to E_G$ and define the parameter E_G. The fitted E_G appears to be about 0.65 eV. It coincides for all InN samples within the accuracy of the model used. Being aware of some uncertainties in a similar estimation procedure with Eq. (1) for reference heavily doped n-GaAs, it is safe to say that the E_g of hexagonal InN is between 0.65 eV and the PL band maximum at 0.73 eV in sample 1. The mean value of $E_g \sim 0.7$ eV is slightly smaller than that suggested by the calculations [1]. The electron concentrations n (cm^{-3}) calculated from the Fermi energy $E_F = 16.6\,(m_0/m^*)\,(n \times 10^{-19})^{2/3}$ meV for an isotropic conduction band with effective mass $m^* = 0.1m_0$ agree with Hall measurements. The calculated optical absorption edge shift of n-type InN due to the Burstein–Moss effect is presented in Fig. 1b. It can be seen that the absorption edge shifts considerably as n increases.

Figure 2a shows the PL spectra for In-rich $In_xGa_{1-x}N$ alloys. The PL bands shift toward higher energies with increasing Ga content. We discuss the results without considering a possible spinodal decomposition in the alloy samples with a higher Ga content. The inset in Fig. 2a shows PL spectra for some of the most perfect alloys and the fitted curves. Figure 2b depicts E_G for In-rich $In_xGa_{1-x}N$ vs. alloy composition estimated from X-ray data. This figure also presents the position of the PL band maxima obtained by other authors for Ga-rich $In_xGa_{1-x}N$ alloys. The experimental points in Fig. 2b can be fitted by a smooth curve $E_G = 3.493 - 2.843x - bx(1-x)$ with the bowing parameter $b = 2.5$ eV. This curve should be considered as a rough estimation under the assumption of homogeneity of alloys. The deviations of the data points from the fit curve in Fig. 2b for In molar fractions $0.3 < x < 0.7$ indicate that a possible phase separation in the alloy has to be taken into account. However, in any case it is seen that the data obtained from the PL spectra of $In_xGa_{1-x}N$ layers ($0.36 < x < 1$) confirm the small E_g of InN.

To summarize, the analysis of PL data obtained on non-intentionally doped single-crystalline hexagonal InN leads to the conclusion that the true band gap of InN is $E_g \sim 0.7$ eV. This finding is supported by studies of the PL bands in In-rich $In_xGa_{1-x}N$ alloys. Our conclusions are also confirmed by first-principles calculations of the InN band gap. The discrepancy with the earlier data on E_g can be explained by the improved quality of InN layers. This explanation is supported by

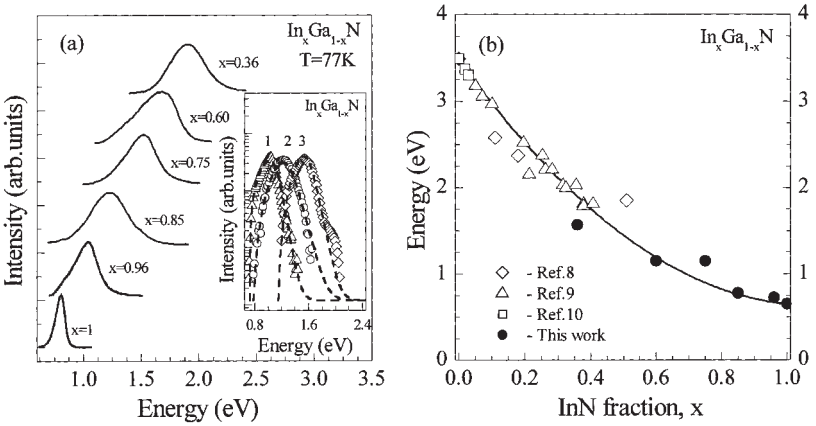

Fig. 2. a) PL spectra of In-rich $In_xGa_{1-x}N$ layers at $T = 77$ K. The inset shows semilog PL spectra and fitted curves obtained from Eq. (1) for most perfect alloys: $x = 0.96$ (1), $x = 0.85$ (2), and $x = 0.75$ (3). b) E_G estimated for In-rich alloys studied in this work, and positions of PL band maxima in Ga-rich alloys taken from Refs. [8–10] as a function of $In_xGa_{1-x}N$ composition

our study of InN samples with E_g of 1.8 eV, which, according to X-ray and Raman data, have a polycrystalline structure and Hall concentrations of electrons exceeding 4×10^{20} cm^{-3}.

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