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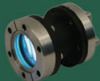



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Optical bandgap energy of wurtzite InN

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Wurtzite InN films were grown on a thick GaN layer by metalorganic vapor phase epitaxy. Growth of a (0001)-oriented single crystalline layer was confirmed by Raman scattering, x-ray diffraction, and reflection high energy electron diffraction. We observed at room temperature strong photoluminescence (PL) at 0.76 eV as well as a clear absorption edge at 0.7–1.0 eV. In contrast, no PL was observed, even by high power excitation, at ~1.9 eV, which had been reported as the band gap in absorption experiments on polycrystalline films. Careful inspection strongly suggests that a wurtzite InN single crystal has a true bandgap of 0.7–1.0 eV, and the discrepancy could be attributed to the difference in crystallinity. © 2002 American Institute of Physics.

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GaN, AlN, and InN have recently attracted great interest and are intensively studied as materials for bright light emitters that cover continuously from the ultraviolet to near-infrared region by proper alloying.¹ Among them, InN remains the most mysterious compound, due mainly to difficulty in growing high-quality crystals because of the extremely high equilibrium vapor pressure of nitrogen. A typical issue is the fundamental band gap E_g . Early absorption studies on polycrystalline films grown by dc discharge,² reactive cathodic sputtering,³ or by rf sputtering,⁴ and a recent rf sputtering study⁵ reported $E_g = 1.8$ – 2.0 eV at room temperature. All of those samples showed, however, no corresponding band-edge photoluminescence (PL). It was quite recently that band-edge emission was observed below 200 K in InN layers grown on Si by molecular beam epitaxy (MBE).⁶ The emission peaks observed at 1.81–2.08 eV were interpreted as a mixture of hexagonal and cubic InN components. To our understanding, however, none of these results showed conclusive evidence of $E_g \sim 1.9$ eV in high-quality single crystals of InN.

We previously reported,⁷ based on a series of absorption experiments on high-quality wurtzite $\text{In}_x\text{Ga}_{1-x}\text{N}$ films, that E_g decreased monotonically from 3.4 eV ($x=0$) to 2.1 eV ($x=0.42$), and pointed out that InN single crystals would have much smaller band gap than commonly believed (~1.9 eV) based on early experiments. Actually, $E_g \sim 0.9$ eV has been reported in a quite recent paper⁸ using high-quality InN films grown by MBE in experiments on PL and PL excitation at low temperature and absorption.

Here, we present experimental evidence that further supports the existence of a similar band gap in high-quality InN

films grown by metalorganic vapor phase epitaxy (MOVPE). At room temperature, we have observed strong band-edge PL peaks at 0.76 eV as well as a clear absorption edge at 0.7–1.0 eV.

The samples were grown by a two-step MOVPE at ambient pressure with a structure of InN (0.1–0.2- μm -thick)/GaN (1.6- μm -thick)/sapphire (0001). The growth temperature was 1010 °C for GaN and 500 °C for InN. Trimethylindium (TMI), trimethylgallium (TMG), and ammonia were the source gases, and the flow ratio of ammonia to TMI (V/III ratio) was 6.2×10^5 during the InN growth. At this growth temperature, ammonia decomposes by less than 0.1%. As a carrier gas, nitrogen was used instead of hydrogen to promote ammonia decomposition. Following our established procedure,⁷ single-crystal growth of a (0001)-oriented hexagonal InN layer was carefully confirmed by reflection high energy electron diffraction (RHEED) and ω - 2θ scan of x-ray diffraction (XRD). Surface morphology was observed by optical microscopy. A confocal Raman microprobe was employed to observe the crystallinity of the InN layer. PL and absorption experiments were carried out to examine the fundamental band gap.

The samples were brownish in color. Observation with an optical microscope in interference derivative mode showed excellent surface morphology with no In droplets. This was in line with the results of XRD, in which the In (101) signal, which is often observed when indium segregated, was below the detection limit. XRD also showed that the samples did not include the cubic phase component.

Figure 1 shows a typical Raman spectrum at room temperature observed by backscattering from the grown surface using the Ar^+ laser at 514.5 nm. Except for a weak but sharp phonon signal from the underlying GaN layer at 568 cm^{-1}

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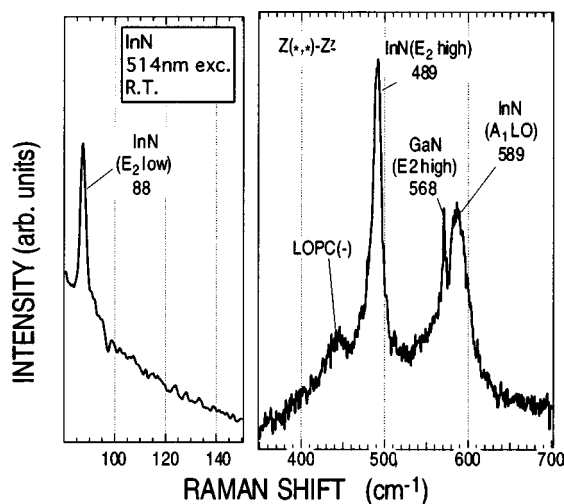


FIG. 1. Raman spectrum of the specimen at room temperature.

(E_2 -high frequency mode),⁹ the spectral features resemble very well those of the highest-quality (0001)-oriented InN films reported¹⁰ in the sense that phonon modes A_1 [longitudinal optical (LO)] at 589 cm^{-1} , E_2 at 489 cm^{-1} (high frequency mode) and at 88 cm^{-1} (low frequency mode) were clearly observed along with an LO-phonon-plasmon-coupled mode (LOPC) at $\sim 440\text{ cm}^{-1}$. Comparison of LOPC with a previous report¹⁰ suggests that the InN layer has a high carrier concentration of $n = 5 - 10 \times 10^{19}\text{ cm}^{-3}$. The observation of the nearly uncoupled A_1 (LO)-phonon mode at 589 cm^{-1} indicates, on the contrary, the existence of a fairly low-carrier-density region. Such coexistence of low- and high-carrier-density regions is commonly observed in recent high-quality InN epitaxial layers and remains a kind of mystery.¹⁰ Highly oriented characteristics were confirmed also by polarized Raman scattering; crossed polarization geometry prohibited A_1 (LO) and LOPC modes, while parallel polarization allowed all the phonon modes in accordance with the Raman selection rule.⁹

A typical result of the absorption experiment is shown in Fig. 2, which plots as absorbance squared versus photon energy. Extrapolation of the linear region I to the horizontal axis gives the band gap of $E_g \sim 3.4\text{ eV}$. Region I is thus attributed to the underlying GaN layer. On the contrary, region II gives $E_g = 0.7 - 1.0\text{ eV}$, which should be ascribed to the InN layer. The latter value was not rigorously determined

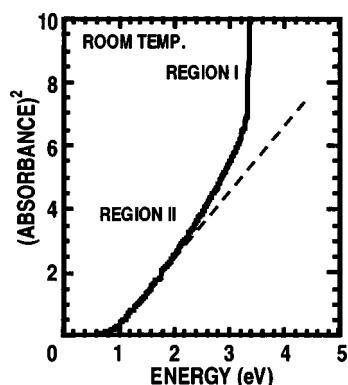


FIG. 2. Absorbance squared vs photon energy at room temperature.

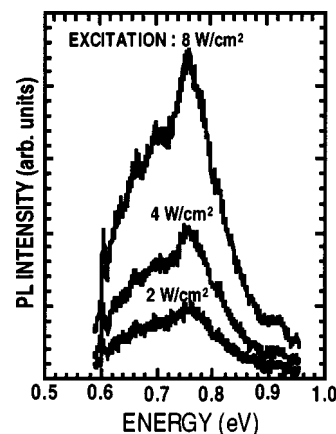
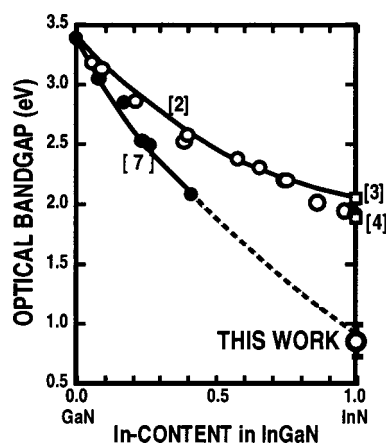


FIG. 3. PL characteristics at room temperature.

because of the strong absorption tail of region I from the thick GaN layer.

Figure 3 shows PL spectra observed for different excitation powers. The experiment was carried out at room temperature using a YAG laser at $1.06\text{ }\mu\text{m}$ wavelength (1.2 eV) with excitation power of $2 - 8\text{ W/cm}^2$, and an InGaAs photodetector with a cutoff wavelength of $2.05\text{ }\mu\text{m}$. When the excitation power was changed, the PL peak energy stayed constant at 0.76 eV , while the peak intensity varied in proportion to the excitation power. The PL spectral line shape will be discussed in detail elsewhere. From the data in Figs. 2 and 3, we consider that Fig. 3 shows a near-band-edge emission. Although we carried out high-power excitation at more than 0.6 MW/cm^2 at 372 nm (3.3 eV), no PL was observed near the previous “band gap” energy ($\sim 1.9\text{ eV}$), except for the InN luminescence as shown in Fig. 3 and a weak yellow band emission from the GaN layer. To conclude, our results strongly suggest that optical band gap of InN should be $0.7 - 1.0\text{ eV}$. Figure 4 plots the reported band-gap energy of $\text{In}_x\text{Ga}_{1-x}\text{N}$ versus In content,^{2-4,7} along with the present result. It is clear that our data on single crystal alloys⁷ will be smoothly connected to the present pure-InN data, and the polycrystalline films²⁻⁴ show larger band gaps than single crystals. The discrepancy could be due to the difference in crystallinity.

Wurtzite InN films grown on a thick GaN layer by MOVPE showed well-oriented single crystals with high

FIG. 4. The relation between In content and the band-gap energy of $\text{In}_x\text{Ga}_{1-x}\text{N}$.

crystallinity, as confirmed by confocal micro-Raman scattering, XRD, and RHEED. An absorption edge at 0.7–1.0 eV and strong PL signals at 0.76 eV were observed at room temperature. These results suggest that the optical band gap of InN should be 0.7–1.0 eV. The discrepancy from previous data could be due to the difference in crystallinity. The band-gap energy of InN will be detailed more in a forthcoming paper.

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