

Unusual properties of the fundamental band gap of InN

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The optical properties of wurtzite-structured InN grown on sapphire substrates by molecular beam epitaxy have been characterized by optical absorption, photoluminescence, and photo-modulated reflectance techniques. All these three characterization techniques show an energy gap for InN between 0.7 and 0.8 eV, much lower than the commonly accepted value of 1.9 eV. The photoluminescence peak energy is found to be sensitive to the free electron concentration of the sample. The peak energy exhibits very weak hydrostatic pressure dependence, and a small, anomalous blueshift with increasing temperature.

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Group III-nitrides are now a widely studied class of semiconductor materials. Both GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ with small x are very efficient light emitters, even in samples with relatively high densities of structural defects, and are used as component layers in a wide range of opto-electronic devices [1]. In contrast, InN has been observed to date to be a very poor light emitter. Early studies of the interband optical absorption performed on InN thin films deposited by sputtering techniques [2,3] and metalorganic vapor phase epitaxy [4] were interpreted as being consistent with a fundamental energy gap of about 2 eV. This value of the band gap has been widely accepted and frequently used as the end point value for the extrapolation of the band gap in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys [5]. It should be emphasized that despite extensive efforts, no light emission associated with the energy gap near 2 eV has ever been reported in these early studies of InN. Only most recently weak photoluminescence peaks with energies ranging from 1.81 eV to 2.16 eV were observed on InN grown on Si substrates [6].

Recent improvements in epitaxial growth techniques have led to the availability of InN films with considerably lower electron concentrations and much higher electron mobilities. Electron concentrations in mid 10^{18} cm^{-3} with room temperature electron mobilities well in excess of $1000 \text{ cm}^2/\text{Vs}$ were achieved by these methods [7-9]. It has been reported most recently that those improved InN films show a relatively strong photoluminescence (PL) at energies around 1 eV [8,9]. Since it has been also found that the position of the PL energy correlates with an onset of strong absorption, it has been argued that the optical transition at about 1 eV corresponds to the fundamental band gap of InN [9].

Interestingly, a number of first-principles theoretical calculations predict an energy gap for InN of less than 2 eV. As expected, the calculations based on the local density approximation (LDA) severely underestimate the energy gap; these calculations predict that InN is metallic with a negative energy gap of -0.4 eV [10]. A recently developed self-interaction and relaxation-corrected pseudopotential approach predicts a larger gap (1.55 eV); this is still significantly smaller than 2 eV [11]. These low values of theoretical energy gaps cannot be entirely attributed to the limitations of the LDA.

Indeed, a quasi-particle corrected LDA calculation that gives accurate values of the energy gaps in GaN and AlN predicts a gap of only 1.39 eV in wurtzite InN [12].

In this letter we report comprehensive studies of the optical and electrical properties of InN samples grown in two laboratories. Our optical absorption, photomodulated reflection, and hydrostatic pressure and temperature dependent PL results are consistent with an intrinsic fundamental band gap of InN of about 0.8 eV. We also find that the low energy gap exhibits unusual temperature and pressure dependencies.

InN films were grown on (0001) sapphire with an AlN buffer layer by molecular beam epitaxy [13]. The thickness of the buffer layer ranges from 70 nm to 200 nm. The InN layer thickness is between 120 nm to 1000 nm. The details of the growth process have been published elsewhere [13]. X-ray diffraction studies have shown that high-quality wurtzite-structured InN epitaxial layers formed with their c-axis perpendicular to the substrate surface. To confirm the experimental results we have observed from this series of samples, we have also measured the PL signal from an InN sample grown in another laboratory by radio-frequency plasma-excited molecular beam epitaxy, using a low-temperature-grown InN buffer layer [14]. This particular sample will be referred as the Ritsumeikan sample in the following text.

The samples were characterized by conventional optical absorption (abs), photoluminescence and photo-modulated reflectance (PR) spectroscopy techniques. The optical absorption measurements were performed using a 0.5 m single-grating monochromator and a germanium photodiode as the detector. The PL signals were generated in the backscattering geometry by excitation with the 476.5 nm line of an argon laser and were dispersed by a 1 m double-grating monochromator. For the pressure-dependent PL studies, the sapphire substrates were thinned down to $\sim 20 \mu\text{m}$, and the samples were cut into small chips $\sim 100 \times 100 \mu\text{m}^2$ in size and mounted into gasketed diamond anvil cells for the application of hydrostatic pressure. The applied pressure was measured by the standard method of monitoring the red shift of the ruby R1 line. For the PR experiments, quasi-monochromatic light from a halogen tungsten lamp dispersed by a 0.5m monochromator was focused on the sample as a probe beam ($\sim 1\text{mm}$ beam size). A chopped HeCd laser beam (442 nm) provided the modulation.

Fig. 1(a) shows the optical characteristics of a typical InN sample with small electron concentration. The free electron concentration in this sample was measured by Hall Effect to be $5 \times 10^{18} \text{ cm}^{-3}$. The optical absorption curve shows an onset at $\sim 0.78 \text{ eV}$. The absorption coefficient increases gradually with increasing photon energy and reaches a value of more than 10^4 cm^{-1} at the photon energy of 1 eV . This high value of the absorption coefficient is typical for an interband absorption in semiconductors [15]. It is important to emphasize that there is no noticeable change in the absorption in the 1.9 to 2.0 eV region, *i. e.*, in the energy range of previously reported energy gaps in InN [3-5].

Also, as shown in Fig. 1(a), the samples exhibit intense room temperature luminescence at energies close to the optical absorption edge. Finally, the 77 K PR spectrum exhibits a transition feature at 0.8 eV with a shape that is characteristic for direct gap interband transitions. The PR feature has a long tail on the higher energy side, which implies considerable oscillator strengths for the interband transition at off-zone-center wavevectors. As with the absorption spectrum, there is no discernible change in the PR signal near 2 eV . The simultaneous observations of the absorption edge and PL and PR features at essentially the same energy indicate that this energy position corresponds to the transition across the fundamental band gap of InN.

Fig. 1(b) shows the room-temperature electron mobility, the peak energy of PL and the transition energy determined by PR as functions of electron concentration. The sample with the highest free electron concentration n of $2 \times 10^{20} \text{ cm}^{-3}$ is silicon doped. All the other samples are not intentionally doped. The samples with the lowest electron concentrations have mobilities ***m*** greater than $1000 \text{ cm}^2/\text{Vs}$. It is seen in Fig. 1(b) that the transition energies increase with increasing free electron concentration. This indicates that the transitions from higher-energy occupied states in the conduction band contribute significantly to the PL spectrum.

The temperature dependence of the PL peak energy can be seen in Fig.1(b). The PL peak energy decreases from 300 K to 12 K ; The shift is smaller for samples with higher free electron concentration, ranging from 0.03 to 0.2 meV/K for the samples under investigation. This behavior is in a stark contrast to temperature dependencies of the direct band gap in most semiconductors, where typically a significant reduction of the

band gap is observed with increasing temperature. For example, the band gap of GaN decreases by 65 meV for the temperature increasing from 15 K to 300 K [16].

More detailed studies of the temperature dependence of the PL were carried out on the sample with $n=5.48 \times 10^{18} \text{ cm}^{-3}$ and $\mu=615 \text{ cm}^2/\text{Vs}$. The results are shown in Fig. 2(a) and Fig. 2(b). As can be seen in Fig.2(b), in addition to the small blueshift (nearly linear at $\sim 0.1 \text{ meV/K}$) in the peak energy of the PL, the integrated intensity of the PL decreases by ~ 20 times as the temperature is increased from 12 K to room temperature. The data in Fig. 2(a) also shows a considerable increase of the linewidth of the PL spectra. The FWHM increases from 35 meV to 70 meV when the temperature increases from 11 K to 300 K. It can be therefore concluded that there is no significant shift of the PL spectra, as the temperature induced line broadening can easily account for the observed small upward shift of the PL line maximum.

We also measured the laser excitation power dependence of the PL. As shown in Fig.3(a), the integrated PL intensity depends linearly on the excitation power over three orders of magnitude. The peak energy does not shift over this excitation energy range. The lack of any PL signal saturation effects again suggests that the PL originates from fundamental interband transitions in InN.

To further elucidate the nature of the observed PL emission, we have studied its hydrostatic pressure behavior. The PL peak energy as a function of applied pressure is shown in Fig.3(b). The linear pressure coefficient is equal to 0.6 meV/kbar, which is considerably smaller than the pressure coefficient previously observed in other III-V compounds. For example, the pressure coefficient of GaN is 4.3 meV/kbar [17], $\text{Al}_x\text{Ga}_{1-x}\text{N}$ is 4.1 meV/kbar for $0.12 < x < 0.6$ [25], and GaAs is 11 meV/kbar [18]. We are aware that the presence of the sapphire, which has a larger bulk modulus than InN, will reduce the degree to which the hydrostatic pressure is transmitted to the InN film, if the film remains coherently strained to the substrate. Using experimental elastic constants for sapphire and theoretical elastic constants for InN, we estimated the correction factor for coherently strained InN on sapphire to be 1.45. Therefore, the pressure dependence of the PL peak energy is between 0.6 meV/kbar and 0.9 meV/kbar. This unusually low pressure coefficient of InN is not totally unexpected since, as it has been shown previously, the

pressure dependence of the energy gap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys decreases rapidly with increasing In content [17, 19].

The small pressure coefficient of the band gap could, at least partially, explain the weak temperature dependence of the band gap. The temperature coefficient of semiconductor band gaps can be decomposed into two contributions, one from the change in the lattice constant due to thermal expansion, and the other one from the electron-phonon interaction [20]. The weak pressure dependence means that there is only a very small contribution of the lattice expansion to the temperature induced band gap change. Also, the small overall temperature coefficient implies that the electron-phonon coupling in this material may be also extraordinarily small.

It should be noted that in addition to the absorption edge at about 2 eV, the early studies of optical properties of InN have also reported onset of strong absorption below 1 eV [3, 4, 21]. This absorption has been attributed to transitions from deep mid-gap defect or impurity levels to the conduction band [21]. Typical optical cross section for deep levels is of the order of 10^{-16} cm^{-2} [22]. Therefore, in order to explain the measured absorption coefficients of more than 10^4 cm^{-1} , it would require the presence of more than 10^{20} cm^{-3} mid-gap defects or impurities. Even if this were the case, one should still be able to see the onset of the valence to the conduction band transitions around the band gap of 2 eV. However, both optical absorption and PR spectra show no indication of any absorption edge in this energy range in our samples, indicating that the previously observed 2 eV absorption edge is not an intrinsic property of InN.

Although the origin of the 2 eV edge is not clear at the moment, it is worthwhile to note that this absorption edge has been especially clearly observed in samples prepared by sputtering techniques. It has been reported that such samples can contain concentrations of oxygen exceeding 10% [23]. Since the reported X-ray diffraction measurement did not detect any crystalline In_2O_3 or any indium oxynitride phases, it was concluded that oxygen is bound in an amorphous indium oxynitride phase. However, another possibility is that oxygen in these materials is incorporated in the form of isolated substitutional defects. Such defects are known to form DX centers with energy levels above the conduction band edge in GaN [24]. It is possible that in InN with large enough oxygen concentrations, these defects form a band. Transitions from and the valence band

to this defect band could be responsible for the “2 eV” absorption edge. This defect related edge is not observed in our MBE grown samples since Secondary Ion Mass Spectroscopy (SIMS) indicates that they have oxygen concentrations $< 10^{19} \text{ cm}^{-3}$.

In summary, we have studied the optical properties of InN layers grown on sapphire by molecular beam epitaxy. The band gap energies of these InN films are observed between 0.7 and 0.8 eV, significantly below values reported previously for InN. The PL peak energy has been measured as a function of free electron concentration, temperature, laser excitation power, and hydrostatic pressure.

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Figure captions

Fig.1 (a) Optical absorption (300 K), PL (300 K), and PR (77 K) spectra of a typical InN sample. This sample is undoped with room-temperature electron concentration of $5.48 \times 10^{18} \text{ cm}^{-3}$. The spike on the PR spectrum at 0.97 eV is an artifact due to the light source used in the PR measurement. (b) Room-temperature mobility, PL peak energy (300 K and 12 K), and the critical energy determined by PR (77 K) as a function of free electron concentration. The sample with $n=1 \times 10^{19} \text{ cm}^{-3}$ (indicated by an arrow) is the Ritsumeikan sample.

Fig.2 (a) PL spectra as a function of temperature for the sample shown in Fig.1(a). The PL spectra are normalized to a constant peak height. (b) The PL peak energy and the PL integrated intensity (log scale) as a function of temperature. The line through the peak energy data is a guide to the eye.

Fig.3 (a) The excitation power dependence of the room-temperature PL integrated intensity for the sample measured in Fig.1(a). (b) PL peak energy as a function of applied hydrostatic pressure.

Figures

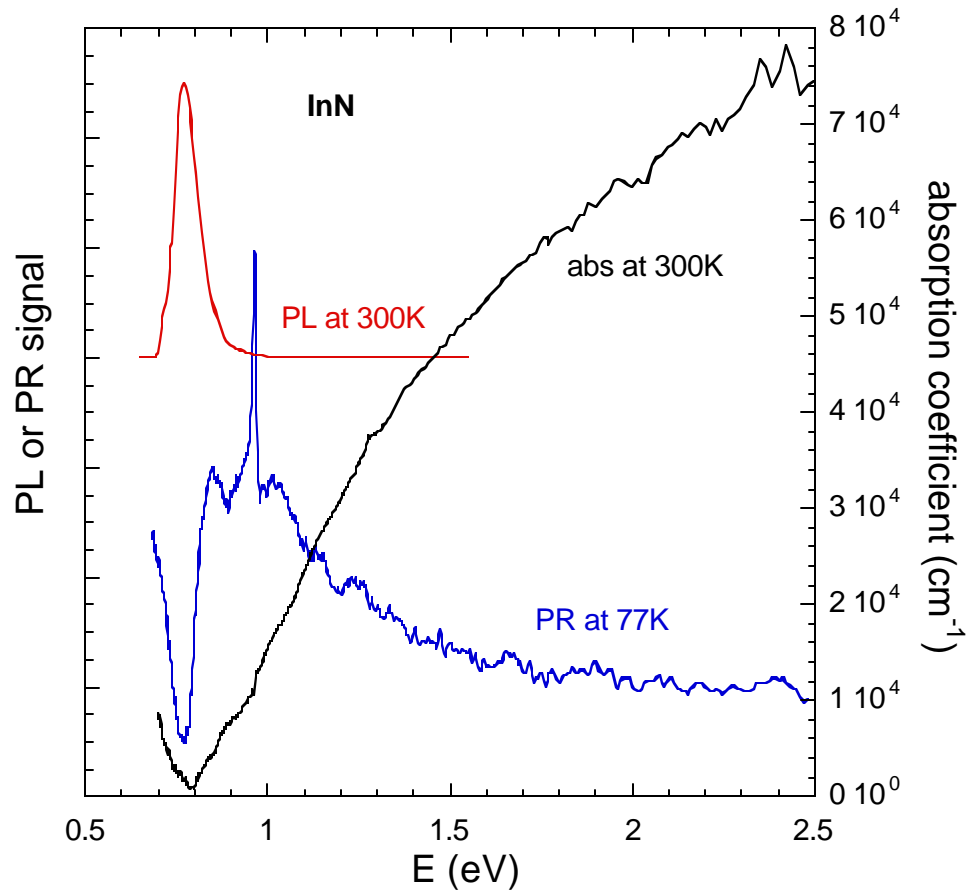


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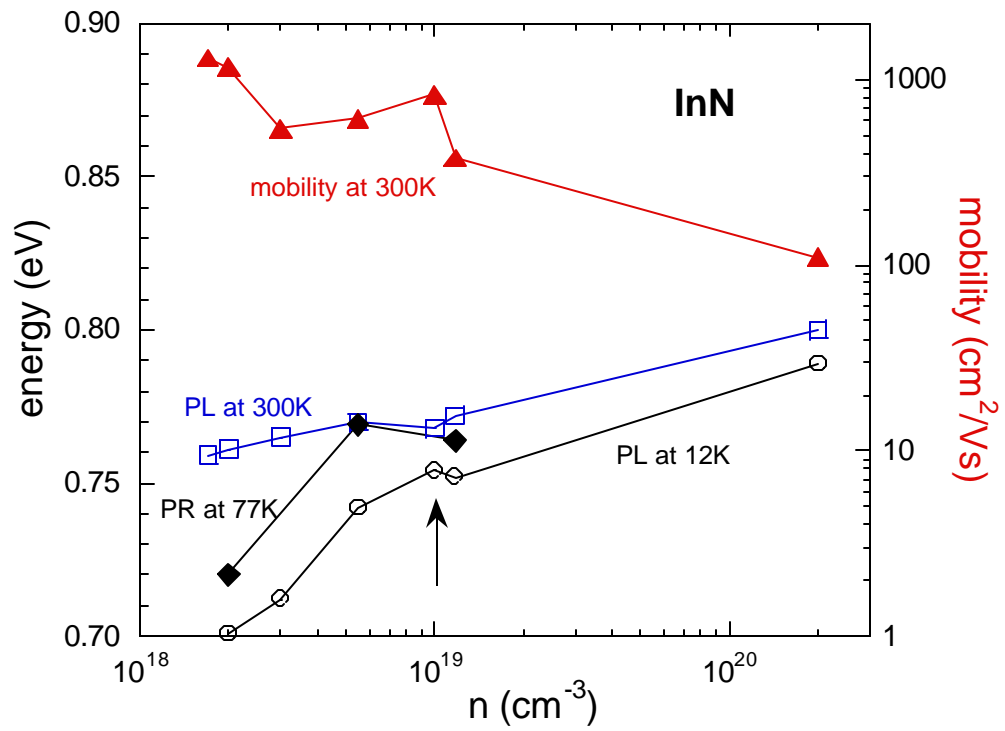


Fig. 1(b) of 3

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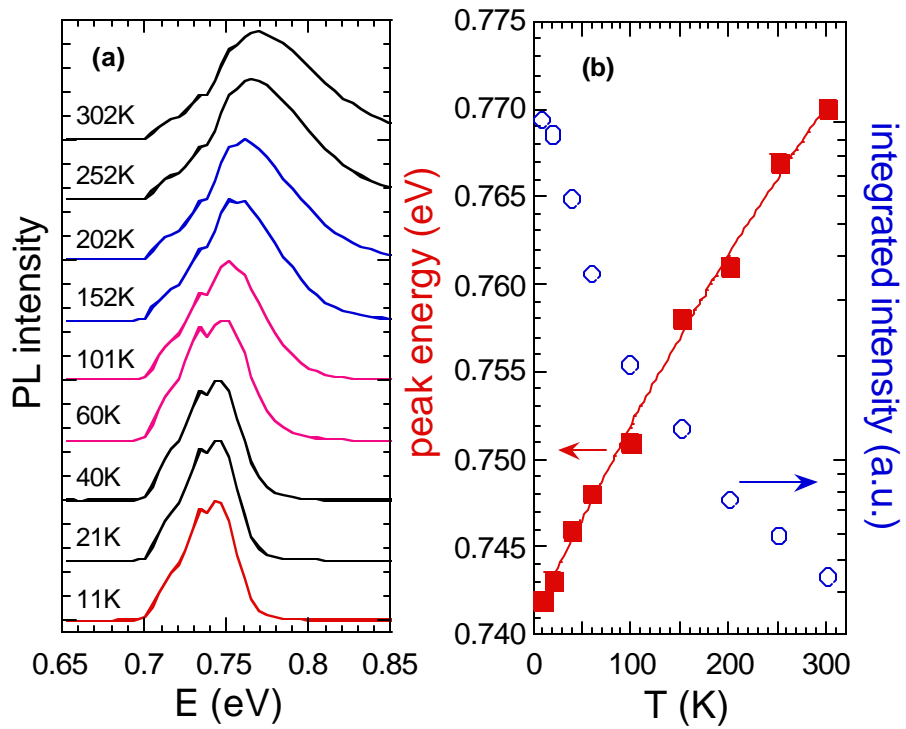


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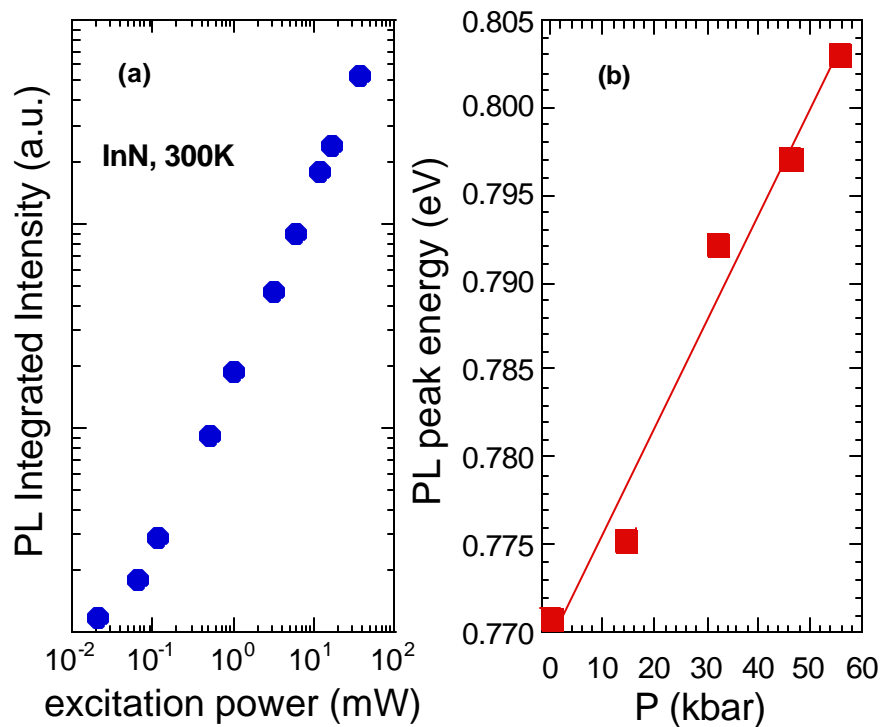


Fig. 3 of 3

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