High resolution transmission electron microscopy of InN

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Hexagonal InN layers were grown by molecular beam epitaxy and studied by high resolution electron microscopy and by photoluminescence spectroscopy. Inclusions of a few nanometers in diameter were found, which are among the smallest reported. Image simulation, beam sensitivity, and photoluminescence of the samples corroborate that these inclusions are indeed metallic indium. This letter provides evidence that nanoscopic metallic indium inclusions can be present in InN crystals and have a strong influence on its optical properties. © 2007 American Institute of Physics.

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III-nitrides are generally considered as wide band gap materials with applications in ultraviolet and visible-range optical devices and high power electronics. It is only recently that measurements suggested a band gap of InN below 1 eV, as opposed to 1.9 eV previously accepted in the literature. However, the structural imperfections and high background doping of InN can result in variation of the band gap. Thus, publications of the last years placed the band gap of InN around 0.6 and 1.9 eV, depending on the employed measurement methods and the analyzed materials. It has been shown that metal clusters could cause resonance in the infrared and affect the photoluminescence (PL) intensity and position. The measurements suggested a band gap of InN below 1 eV, as opposed to 1.9 eV previously accepted in the literature. However, the structural imperfections and high background doping of InN can result in variation of the band gap. Thus, publications of the last years placed the band gap of InN around 0.6 and 1.9 eV, depending on the employed measurement methods and the analyzed materials.

In this letter, we present high resolution transmission electron microscopy (HRTEM) studies of InN showing that inclusions of 5–40 nm can indeed be present in samples of apparent high quality as determined from XRD. Contrast variation and the moiré pattern observed can be explained by the inclusions of metallic indium. Samples with different cluster sizes show a change in the PL intensity and position.

Hexagonal InN epilayers were grown by plasma-assisted molecular beam epitaxy on sapphire, as described elsewhere, at Ioffe Institute using the Compact 21 T setup (France, Riber) equipped by a plasma source HD-25 from Oxford Applied Research Sample rotation was suppressed leading to an inhomogeneous deposition. In particular, with an average substrate temperature of 480 °C, there was an ~20 °C positive temperature gradient from the center to the periphery of a wafer. It should result in an increasing size of metallic inclusions towards the border of the wafer. Indeed, scanning electron microscopy revealed surface indium droplets at the periphery only. These droplets were etched chemically before the TEM and PL investigations. Sample A was taken from the center of the wafer and Sample B was taken from its edge.

The samples were prepared for TEM in cross-section geometry in the {110} and {110} zone axes by mechanical thinning and argon ion milling using a Fischione ion mill operated at 6 keV for milling and 2 keV for polishing. To further reduce surface roughness, the samples were polished in a Linda ion mill on a liquid nitrogen cooled stage using a 500 eV beam. HRTEM images of the samples were recorded on a FEG CM300 operated at 300 keV and close to Scherzer defocus.

After low energy ion milling, both samples show uniform contrast over wide areas indicating a clean and flat surface. Only the hexagonal phase is detectable. However, nanometer size areas of contrast were seen, as shown in Fig. 1. This contrast is not due to electron beam damage, as the inclusions have been found in areas exposed to the beam in less than 10 s at only 1 A/cm². On the contrary, contrast alteration appears only after a few minutes of beam exposure causing contrast of the inclusion to disappear. The inclusions have an extension of about 5–10 nm in sample A and 20–40 nm in sample B (Fig. 1). As the size increase is in

![FIG. 1. HRTEM images of (a) sample A showing inclusions of 5–10 nm in size. The inset shows a magnified image of an inclusion. (b) Sample B showing inclusions of about 20 nm in size. Moiré pattern visible on the lower left side of the cluster is compatible with tetragonal metallic indium.](https://example.com/fig1.png)
accordance with the growth mode and the samples were prepared in identical manner, we are confident that contrast imaged in the first seconds of illumination is due to inclusions that are already present inside the original material. The inclusions found are much smaller than any of the inclusions reported to date in InN.6

Figure 2 shows a high resolution image of an inclusion together with power spectra from the indicated areas. No additional spots can be seen in the power spectrum of the inclusion. However, the spots are broadened by strain, which indicates that the inclusion is contained in the matrix as opposed to sitting on the sample surface.

According to the lattice parameters given in the Pearson’s Handbook,8 the lattices of hexagonal InN and tetragonal indium have similar diffraction patterns if \( \frac{1}{201} \) and \( [2 \overline{1} 0] [200] \) resulting in 5% and 9% lattice mismatches, respectively. (Note that indium also appears in a cubic phase for nanoparticles, see, e.g., Ref. 9). Figure 3 shows a calculated image at Scherzer defocus of an extended unit cell of InN \([110]\) of 10 nm thickness containing a 4 \( \times \) 4 \( \times \) 4 nm\(^3\) inclusion of tetragonal indium simulated with the program MACTEMPAS.10 A darker contrast at the center corresponds to the indium inclusion. Fourier transforms were taken in a similar manner to Fig. 2 showing that no additional diffraction spots may be observed if the inclusion is oriented along the matrix material. Simulations in the \([\overline{1}00]\) direction give identical results.

However, the effects of lattice mismatch become noticeable in the larger inclusions through interference with the host lattice. Figure 1(b) shows such a moiré pattern in the lower left corner. Simulations of superimposed layers of hexagonal InN and tetragonal indium with the mentioned orientation relationship do indeed predict moiré pattern with a period of about 8 nm along the c axis and down to a few nanometers when rotated that can explain the moiré pattern with indium inclusions under strained conditions. Their period is too large to be observed in the small inclusions of sample A. Indeed, spectroscopic TEM studies of the samples confirmed the existence of indium in sample B (Ref. 11) and place the band gap of defect-free InN around 1.7 eV.12

The beam sensitivity of the inclusions upon beam exposure is quite peculiar as they disappear in a few minutes even under very low beam currents (1 A/cm\(^2\)). Beam damage generally appears in the form of knock-on damage or through ionization. In nitrides, high energetic rays ionize nitrogen atoms which then diffuse through the host crystal until they find another nitrogen radical and combine to N\(_2\) to leave the crystal. If there is no nitrogen radical in the vicinity, the atom is caught by the host crystal in its initial site or on an interstitial.13,14 The nitrogen radicals can be trapped inside the indium clusters and eventually, the inclusions will contain as much nitrogen as the matrix, attenuating the contrast. The effect of beam damage in InN will be discussed in depth in a separate paper.

Figure 4 shows the PL spectra of the two studied samples. The PL emission in sample A with its small clusters is centered at 0.6 eV and is about one order of magnitude weaker than in sample B centered at 0.68 eV. The spectra are similar to those observed before cleaving the wafer holding samples A and B; a uniform Fermi level thus excludes a different Moss Burstein shift. The samples were grown and prepared under identical conditions except for a temperature gradient causing a change in size of the inclusions. Therefore, Fig. 4 shows the drastic effect of inclusions on the optical properties of InN.
The modification of the PL spectra can be understood if we remind two basic phenomena which are possible in metallic In inclusions—the plasmonic (Mie) resonances and the specific interband absorption between the parallel bands in metallic indium.\textsuperscript{15} Such absorption starts from $\sim 0.6$ to $0.7$ eV, reaching maximum at $0.9$–$1.5$ eV.\textsuperscript{16} The Mie resonance depends strongly on the aspect ratio of the inclusions. A high aspect ratio can shift the resonance into the infrared. However, the HRTEM images do not indicate high aspect ratios. If the inclusions are presumed to be spherical, they would produce Mie resonances near $2.8$–$3$ eV. Additionally, in small clusters (5 nm) the damping of the resonances by boundaries should be significant. Thus we assume that the basic optical effect in the small clusters is the parallel band absorption. It has been previously demonstrated that such absorption can quench the infrared PL near $0.7$ eV, while in the larger clusters some plasmon-induced enhancement of the emission is possible.\textsuperscript{5}

Even in almost spherical clusters, it can be due to the local increase of electromagnetic field at sharp corners.

Due to similar crystal parameters, it may be argued that the inclusions could contain a cubic phase InN. However, the contrast change stemming from these inclusions is weaker than from pure indium. More importantly, cubic InN is expected to have a lower band gap than the hexagonal phase. Cubic InN clusters would thus act as localization centers for charge carriers (quantum dots). Sample A with smaller inclusions is then expected to have a higher-energy shift of PL due to possible confinement; sample B should have a lower-energy shift. This is in direct contradiction with the luminescence spectra shown in Fig. 4. Another common precipitate in InN is In$_2$O$_3$;\textsuperscript{17} however, the oxide has been related to high band gap transition in InN (Ref. 4) and cannot explain the different PL observed in the studied samples.

In conclusion, we have demonstrated nanometer-scale inclusions in two InN samples by HRTEM imaging and PL spectroscopy. Careful sample preparation produced damage-free, flat surfaces where changes in contrast and moiré pattern are explained by metallic indium clusters. Due to an increase in growth temperature, the size of the inclusions is about 5 nm in sample A and about 20 nm in sample B. Furthermore, it is established that the variation in the cluster sizes is consistent with modification in infrared luminescence, induced mostly by specific interband absorption within the metallic indium. In summary, nanoscopic metallic indium inclusions can be present in InN and cause a significant change in optical properties.

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