Mie Resonances, Infrared Emission, and the Band Gap of InN

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Mie resonances due to scattering or absorption of light in InN-containing clusters of metallic In may have been erroneously interpreted as the infrared band gap absorption in tens of papers. Here we show by direct thermally detected optical absorption measurements that the true band gap of InN is markedly wider than the currently accepted 0.7 eV. Microcathodoluminescence studies complemented by the imaging of metallic In have shown that bright infrared emission at 0.7–0.8 eV arises in a close vicinity of In inclusions and is likely associated with surface states at the metal/InN interfaces.

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InN is one of the most mysterious semiconductor materials studied up to now. While it has been carefully investigated since the 1980s using all the modern spectroscopic techniques, the band parameters of InN (gap energy, effective masses) are still under debate. This uncertainty is particularly embarrassing since InN-containing heterostructures have a huge potentiality for lasers, white-light diodes, and other devices.

In this Letter we show that dramatic deviations in presently available experimental data on the band gap of InN from 0.7 to 2 eV [1–4] have a fundamental physical reason. They are linked to the precipitation of indium in the metallic phase that leads to additional optical losses associated with Mie resonances.

Resonant light scattering and absorption by dispersed small particles, described by Mie almost 100 years ago [5], have been thoroughly investigated in different objects in nature—cosmic dust, comets, atmosphere clouds, etc. (see, e.g., Ref. [6]). They have also been repeatedly observed in various dielectrics and semiconductors with clusters of different metals [7,8]. These phenomena arise from the interaction of an incident electromagnetic wave with multipolar excitations of electrons in the clusters.

Such effects have been neglected in studies of InN, although it is well known that the poor thermal stability of InN and low In vapor pressure over the metal phase result in the formation of In clusters [9], especially at temperatures $T > 500\,^{\circ}\mathrm{C}$. A good correlation between the recently registered infrared (IR) photoluminescence (PL) and the optical absorption edge has been considered as a doubtless evidence of the narrow gap.

We have examined two representative sets of InN epilayers grown by both plasma-assisted molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) on sapphire and other substrates. The maximum of the IR emission in these samples has been registered in the 0.7–0.8 eV range independently of the growth technique and the way of excitation, i.e., optically, by different laser lines, or by an electron beam in the cathodoluminescence (CL) study (Fig. 1). The latter has been performed at 5 K in a LEO 1550 Gemini analytical scanning electron microscope.

The electron concentration in the samples, as determined by IR ellipsometry measurements, varies from 2.1

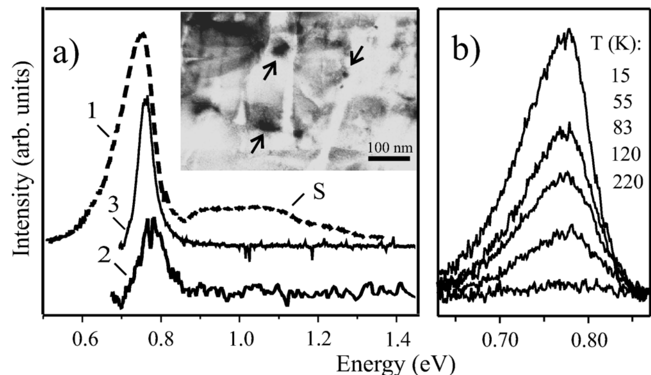

FIG. 1. (a) Spectra of (1) PL excited by an InGaAs laser in an InN sample grown by MBE (registration by a combination of InGaAs and PbS detectors); CL spectra registered in (2) the same MBE sample and (3) a MOCVD sample. The Ge detector cuts the long-wavelength tail of the CL. "S" indicates scattered signal (see text). The inset presents a cross-sectional TEM micrograph of an MBE sample with In precipitates marked by arrows. (b) PL temperature behavior in the MBE sample (PbS detector).

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up to 8.4×10^{19} cm^{-3}, assuming an effective electron mass of $m_e^* = 0.11 m_0$ [10]. No noticeable correlation between the IR emission energy and the carrier concentration was observed. A shift of the PL with a temperature rise is very small [Fig. 1(b)], similar to previous reports [11].

The samples studied may be divided into three groups with (A) bright, (B) weak, and (C) negligible IR emission [Figs. 2(a)–2(c)]. Among 18 layers only three, grown with $T > 500\,^{\circ}$C, belong to group A. Most of the samples either do not emit light at all or show a weak signal, in spite of reasonable structural quality. All the samples exhibiting the IR PL contain inclusions of a tetragonal In phase in hexagonal InN, as revealed by x-ray diffraction (XRD) measurements. The In precipitates have been directly observed in a transmission electron microscopy (TEM) image as well (Fig. 1, inset). As can be seen in Fig. 2, the IR PL energies are almost independent on the metal content, while the PL intensity correlates with that of the (101) In peak. Both are most enhanced in samples A and quenched in samples C.

We have studied whether there is any spatial correlation between the IR emission and the distribution of metallic In. This has been done in the same analytical microscope using a detector of backscattered electrons (BSE), sensitive to atomic weight, and an energy dispersive x-ray (EDX) analyzer.

Figures 3(a)–3(d) summarize the results of the studies for an MBE sample A. It turns out that the IR CL arises within the In-enriched regions, visible as bright areas in both a BSE image and mapping of In x-ray fluorescence. This CL is dotty, while emission from sapphire (not presented here), penetrating between the In-enriched regions at ~8 kV, is homogeneous. Moreover, the spots of the IR CL coincide most frequently with specific defects, well resolved in the secondary electron (SE) images, which are, in fact, dips in the InN films above the contacts with the metal particles. In MOCVD samples A, the precipitates of metallic In are observed between the boundaries of hexagonal grains in both SE and BSE images. Accordingly, the IR CL looks like a fine net along the grain boundaries (Fig. 4).

In samples B, with the smaller In content, the distribution of IR emitting spots in the CL images is more homogeneous. Their density and average size (~ 100 nm) are smaller than in sample A. These CL spots appear on the In agglomerations which have almost circular shapes. In the samples C without noticeable traces of indium [Figs. 3(e) and 3(f)], we failed to register the luminescence at all. Obviously, the bright IR (0.7–-0.8 eV) emission in both MBE and MOCVD sets of the samples is associated with the In aggregates.

Total optical extinction losses in a semiconductor matrix with metallic clusters, besides the interband absorption in the matrix, contain two additional components: (i) true (bipolar) absorption or transformation of radiation energy into heat in small particles, and (ii) resonant scattering on plasmon excitations, which is important for larger particles [7]. Characteristic features of both components are observed in our optical spectra.

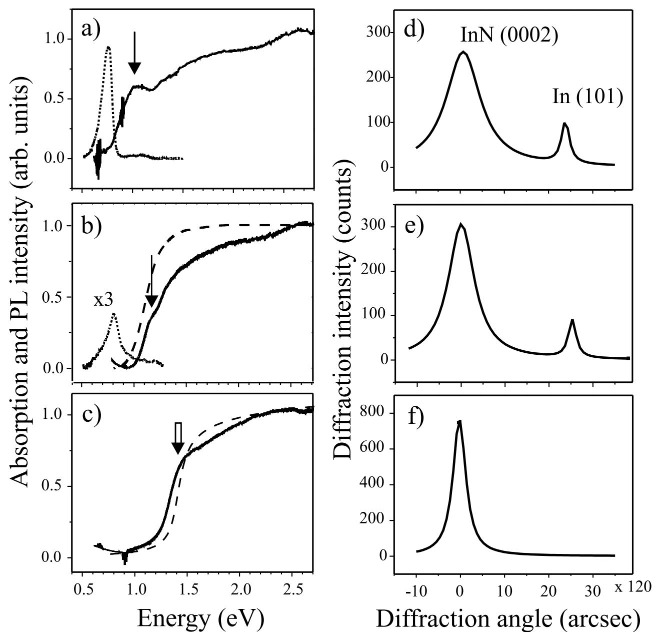

FIG. 2. TDOA (solid lines), IR PL (dotted lines), and optical absorption (dashed lines) spectra taken in MBE grown InN films with (a) high, (b) moderate, and (c) negligible concentration of metallic In. Respective XRD scans are shown in (d)–(f). Vertical single arrows indicate an additional absorption peak (see text); the double arrow denotes the position of the InN band edge, as determined by the TDOA.

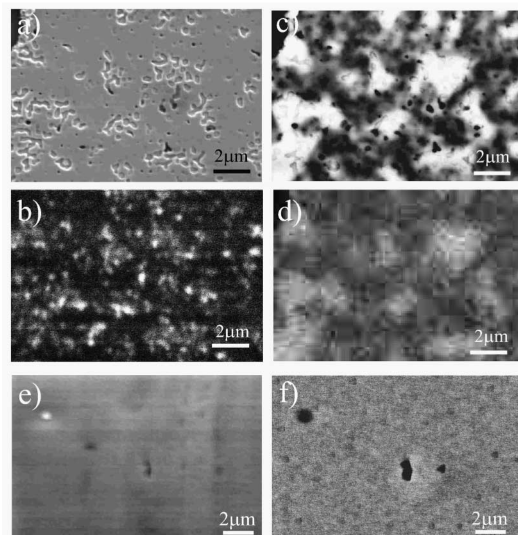

FIG. 3. Images registered at the same spot of the MBE sample A: (a) SE at 5 keV; (b) CL at 4.3 kV, (c) BSE at 20 keV, (d) In mapping in an energy window of 3.287–3.487 kV (InLa1 and InLb1). White regions in (c) and (d) are In enriched. Images (e) SE and (f) BSE are taken at 20 keV in the MBE sample C where the IR CL has not been registered.

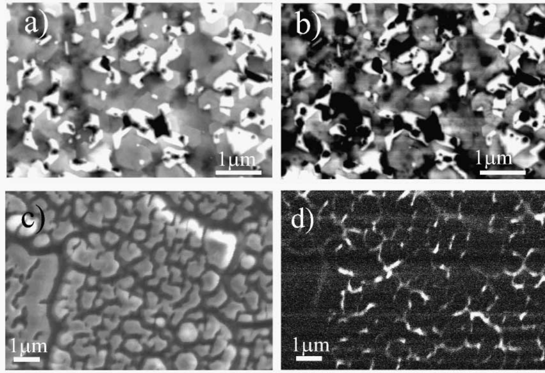

FIG. 4. Typical (a) SE and (b) BSE images registered at 20 keV in the MOCVD sample A. White inclusions between hexagons are metallic In. (c) SE and (d) CL images taken at 4.85 kV in this area.

The PL spectra often contain an additional "S" band above the main one, in the 0.8–1.4 eV range [Fig. 1(a)]. Our study has shown that this is the contribution of an abnormally strong scattered background signal (nonmonochromatic spontaneous emission of the semiconductor laser and/or fluorescence of all optical components at high excitation power). Apparently, the scattered signal is absent in the CL spectra due to the electron beam excitation without such a background. At the normal incidence, the signal may be so strong that it masks the real IR emission. This scattering can falsify the results of conventional optical absorption measurements as well, since less optical energy reaches the detector.

To distinguish between such optical losses and true absorption we have used the thermally detected optical absorption (TDOA) technique. This method, suitable for thick or holed layers, is performed at 0.35 K. It is based on the detection of a small increase in the sample temperature, which is proportional to true absorption [12]. In our case, the increase arises from the creation of phonons at nonradiative recombination activated by the initial interband optical absorption and from the bipolar absorption of light in the metallic particles.

In contrast to the optical absorption which is smooth and extends to lower energies in the layers with the clusters, the TDOA features complicated spectra with a pronounced additional peak below a principal absorption edge. This peak being strong in samples A disappears completely in samples C, where the clusters are not detected (Fig. 2). Therefore, we consider the peak to be associated with the absorption within them. The sharpness of the resonance is related to the extremely low temperature at the measurements, which prevents broadening induced by electron-acoustic phonon scattering.

In the classical Mie theory [5], the extinction losses for a metallic sphere depend on the complex dielectric functions of both matrix material (ϵ) and metal (ϵ_m). As a result, the resonance energy of the In clusters immersed in InN ($\epsilon_0 \sim 8.4$) is significantly lower than that in vacuum. Besides, qualitative EDX analysis has shown that there is an excess of In of a few percent in our samples. Such a filling factor f should significantly change the complex dielectric function of any semiconductor. The shape of In inclusions is far from spherical and their distribution is not random. They are predominantly formed either between columns or at an interface with a substrate, being extended in the growth direction or in plane, respectively. To take the factors into account, we have used the model based on the Maxwell-Garnett approximation for an effective medium [13], developed for nonspherical metal particles in an absorbing matrix [8]. In this model, the total absorption is given as

$$\alpha \propto \mathrm{Im}[\epsilon(w)G(w)],$$

where

$$G(w) = \left(1 + f\frac{(\epsilon_m - \epsilon)(1 - L_m)}{L_m\epsilon_m + (1 - L_m)\epsilon}\right) \Big/ \left(1 - f\frac{(\epsilon_m - \epsilon)L_m}{L_m\epsilon_m + (1 - L_m)\epsilon}\right).$$

Here L_m denotes the depolarization factor, which equals 0.33 for spheres. The complex dielectric function for indium is taken from Ref. [14]. Currently, there is uncertainty in the InN complex dielectric function. We take it from Ref. [15] for the sake of demonstration.

Our calculation has shown that the resonance absorption energy in the InN/In composite can shift down to the IR range, as a result of the increased In content and the shape variation. For instance, the pronounced peak at 1 eV in the experimental TDOA spectrum (Fig. 5) corresponds to the resonance in the clusters with $L_m = 0.07$. Such a small L_m value means that the respective clusters are elongated along the light propagation direction, like the intercolumn indium inclusions. In this case, the depolarization is small, and the resonance energy is lowest among possible [16]. This type of the clusters determines the effective absorption edge in InN. The resonances of the clusters with $L_m \geq 0.33$ are higher in energy than the absorption edge in InN, so the oblate interface inclusions do not affect the effective band edge. The resonances in the clusters of intermediate shapes fill the gap between the lowest resonance and the InN edge. They are suppressed partially by intrinsic In absorption at ~1.4 eV.

One should clarify that the band gap energy in a TDOA spectrum corresponds to the position of the kink between the constant and the slope parts, which is near 1.4 eV in the InN samples without detectable metallic inclusions [Fig. 2(c)]. It is tempting to conclude that the true band edge of InN is somewhere here, with possible correction on the Burstein shift. However, it is difficult to separate the interband absorption in InN from the Mie absorption

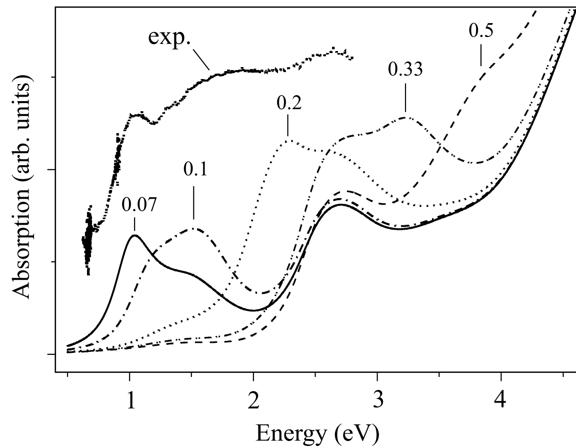

FIG. 5. Absorption spectra in InN with 2% of metallic In calculated for different L_m values marked on the plot. The experimental TDOA spectrum of the MBE sample A is shown for comparison.

in ultrasmall In nanoclusters. Thorough high-resolution TEM studies are needed for that.

The IR emission is situated significantly below the principal edge in TDOA spectra, so it can hardly be attributed to the near-band-edge luminescence. One can assume that it may be related to gap states induced by residual defects, whose formation energies in InN are small [17]. In our samples, however, the emission is not homogeneous, but arises at the interfaces of the indium inclusions with InN. Among the possible mechanisms, recombination involving surface states at an interface metal/semiconductor seems to us the most reasonable. Such type of emission had been observed previously in several III-V compounds with metal coverage [18]. These surface states can be either Tamm states at a contact of a perfect crystal with a massive metal inclusion [19] or deep levels near the interface, induced by residual defects. The energy of the states can be roughly estimated as a difference between the gap width and a potential barrier height at an interface [20]. Based on the experimental data on the surface Fermi level position in InN covered by metals [21], one can expect the surface states 0.7–1.2 eV above the valence band maximum. Thus, the energy of transitions, involving the surface states and holes, is consistent with the registered IR emission energies. The energy, correlating with the barrier height, is weakly sensitive to the band energy variation with temperature, as has been observed.

In conclusion, the presence of In precipitates could explain a lot of experimental data, including the huge band-edge shift, the IR emission, and scattering. The Mie resonances are important for InGaN epilayers as well, because of the observed activation of the In segregation phenomena in the alloys at high growth temperatures. We recapitulate that InN of high quality, grown at $T > 500\,^{\circ}$C, absorbs and emits light far below its band gap due to Mie resonances and surface/gap states, respectively.

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