

Electronic structure of wurtzite and rocksalt InN investigated by optical absorption under hydrostatic pressure

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The pressure dependence of the optical absorption edge of InN is investigated. Owing to the strong nonparabolicity of the energy bands, wurtzite InN exhibits enhanced optical absorption well above the absorption edge. The direct band gap of wurtzite InN increases linearly with pressure at 29 ± 1 meV/GPa. The wurtzite-to-rocksalt phase transition is observed at 15.3 ± 0.5 GPa as a clear change in the absorption edge. We find that rocksalt InN is an indirect semiconductor with a band gap energy of around 1.0 eV. A higher energy direct transition is found at ~ 2 eV. These results are discussed in terms of theoretical band-structure calculations. © 2010 American Institute of Physics. [doi:10.1063/1.3431291]

InN and related group-III nitride alloys are currently being the object of intense investigation because of their potential applications in optoelectronics, photovoltaics, and high-frequency electronics. Over the past few years, research efforts have been devoted to the production of high-quality InN samples with reduced residual electron concentrations. Optical studies in high-quality material led to the discovery of the 0.7 eV fundamental band gap of wurtzite InN (w-InN), much lower than the previously established values ($E_g \sim 2$ eV).¹ The currently accepted band gap value of InN made necessary to revise band-structure calculations and to re-evaluate the material parameters of InN and InN-based alloys, including their pressure behavior.^{2,3}

The application of high pressures is a powerful tool for the study of the electronic properties of semiconductors. High-pressure techniques are also interesting from the point of view of material preparation, since metastable phases with technologically important properties can be obtained after decompression. X-ray diffraction (XRD) and Raman studies have shown that InN undergoes a phase transition to the rocksalt structure (rs-InN) at about 14 GPa.⁴⁻⁶ However, in spite of much research on the fundamental properties and device applications of InN, relatively little is known about the pressure behavior of this compound and in particular about the electronic properties of rs-InN. While only a few experimental works dealing with the high-pressure optical properties of w-InN have been published so far,^{2,7-9} the electronic properties of rs-InN have been only addressed theoretically.¹⁰⁻¹³

In this letter, we focus on the high-pressure optical properties of both w-InN and rs-InN. We report on the pressure behavior of the absorption edge of both phases and show that the band gap of rs-InN is indirect, with a band gap of around 1.0 eV just above the transition pressure.

For this study, we used a nominally undoped, 500-nm-thick InN epilayer grown by plasma assisted molecular beam

epitaxy on a GaN/sapphire template at ~ 450 °C. Repetitions of In droplet elimination by radical beam irradiation were performed during growth to obtain high-quality InN.¹⁴ Standard Hall effect measurements yielded a background electron concentration of 1.8×10^{18} cm⁻³ and an electron mobility of 1340 cm² V⁻¹ s⁻¹. Flakes containing InN/GaN/sapphire were detached from the sapphire substrate by scraping. The thickness of the remaining sapphire layer was 20–30 μm. The flakes were mounted in a gasketed membrane-type diamond anvil cell with 500 μm diameter anvils. Methanol-ethanol-water (16:3:1) was used as pressure transmitting medium. The applied pressure was determined by the ruby fluorescence method. The optical setup for the infrared spectral range included a tungsten lamp, reflecting optics objectives, spatial filters, a single-grating monochromator and a PbS detector connected to a lock-in amplifier. For the near-infrared and visible measurements, multichannel spectrophotometers from Ocean Optics Inc. were employed.

Optical measurements in thin InN epilayers are not very sensitive to the low values of the absorption coefficient $\alpha(h\nu)$ at photon energies $E=h\nu$ around the absorption edge, in contrast to what occurs in thicker films or in bulk samples. Interestingly, the measurements in thinner samples allow one to probe the absorption spectrum at higher photon energies, where important nonparabolicity effects may occur. Figure 1(a) shows some representative room-temperature absorption curves obtained at different hydrostatic pressures from the sample studied in this work. The monotonic blueshift in the absorption edge of w-InN with increasing pressure is clearly observed. Although no exciton-related absorption peaks are observed in the room-temperature spectra, the optical absorption is still enhanced by the Coulomb interaction between electrons and holes and, as a consequence, the analysis of the absorption edge by using the typical $(h\nu - E_g)^{1/2}$ dependence is expected to yield slightly underestimated values of E_g . Apparently, the spectra of Fig. 1 do not exhibit the broadened, steplike spectral shapes predicted by Elliott-Toyozawa theory of excitonic optical absorption in direct

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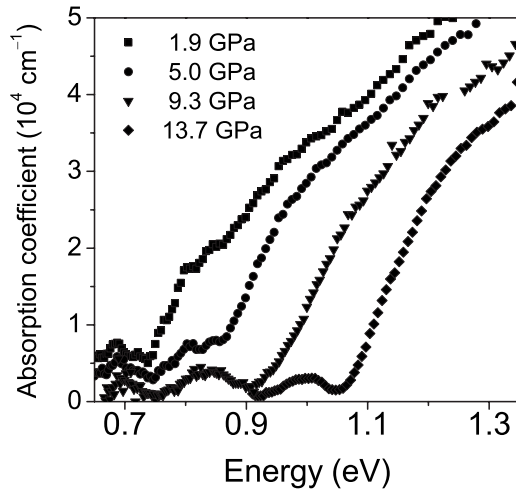


FIG. 1. Absorption edge measured at 300 K for different hydrostatic pressures in a w-InN epilayer.

semiconductors.¹⁵ For energies just above the absorption edge, $\alpha(h\nu)$ increases at a relatively low rate in relation to other semiconductors; this may be related to the lack of excitonic peaks in the absorption edge of InN.² For photon energies above $E \sim E_g + 0.2$ eV the absorption curves display a reduction in slope, which may be linked to the steplike behavior predicted by Elliott–Toyozawa’s theory. However, the observed rate of increase of $\alpha(h\nu)$ (~ 100 cm⁻¹/meV) is sizeably larger than that observed in GaAs [~ 70 cm⁻¹/meV (Ref. 15)] or in wide band gap semiconductors like GaN [~ 65 cm⁻¹/meV (Ref. 16)] or ZnO [~ 35 cm⁻¹/meV (Ref. 17)] well above the absorption edge. As will be apparent below, this observation can be attributed to the strong nonparabolicity of the energy bands of InN.

To determine the direct band gap energy as a function of pressure from the optical data, we have fitted the absorption spectra by using the formalism of Ref. 18, where the absorption coefficient including nonparabolicity effects is given by $\alpha_{np}(h\nu) = \alpha_p(h\nu)[1 - B(h\nu - E_g)]^{-5/2}$, where α_p is the absorption coefficient for parabolic bands and B is a nonparabolicity constant.¹⁸ To obtain $\alpha_p(h\nu)$ we neglect the contribution of discrete absorption lines and we use the analytical expression of Ref. 15 for the exciton continuum. For the nonparabolicity constant B we take a value of 1.05 eV⁻¹, which is consistent with the energy dispersion of the conduction band of InN as obtained from Kane’s two-band $\mathbf{k} \cdot \mathbf{p}$ model¹⁹ and which fairly well reproduces the behavior of $\alpha(h\nu)$ well above the absorption edge (see below).

Figure 2 shows the pressure dependence of E_g in our InN epilayer as obtained from the fits to the absorption spectra. From a least-squares linear fit we extract a pressure coefficient of 29 ± 1 meV/GPa, in very good agreement with the absorption experiments of Ref. 2 on a 7.5- μm -thick epilayer (30 ± 1 meV/GPa) and also with the photoluminescence data of Ref. 8 as obtained from samples with electron concentrations similar to that of our sample (28.2 ± 0.8 meV/GPa). As can be seen in the inset of Fig. 2 for the case of 11 GPa, the calculated absorption curves (solid line) closely follow the experimental data when nonparabolicity effects are taken into account. In contrast, neglecting such effects [i.e., $B=0$ in the expression for $\alpha_{np}(h\nu)$] gives rise to an important underestimation of the absorption

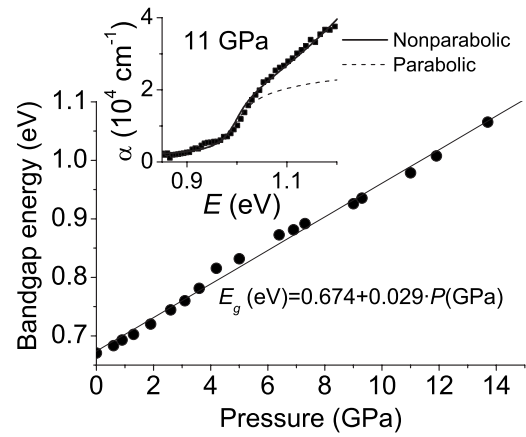


FIG. 2. Pressure dependence of the band gap energy of w-InN as obtained from a fit based on Elliott–Toyozawa theory including nonparabolicity effects. The inset shows the result of a fit to the absorption spectrum acquired at 11 GPa (solid squares) when the nonparabolicity of the energy bands is considered (solid line) and in the case of parabolic bands (dashed curve).

coefficient (dashed curve). This result confirms that the larger rate of increase in $\alpha(h\nu)$ in InN in relation to other semiconductors can be attributed to the strong nonparabolicity of the conduction band of this material.

Figure 3 shows different absorption spectra obtained on the upstroke (curves at 13.7, 15.7, and 25.6 GPa) and on the downstroke (8.9 GPa). In the upstroke cycle the wurtzite-to-rocksalt phase transition is clearly observed as a change in the shape of $\alpha(h\nu)$ (see curves at 13.7 and 15.7 GPa). Interference fringes associated with the GaN buffer layer appear in all these curves. Our measurements suggest that the phase transition is complete at about 15.3 ± 0.5 GPa. This value is somewhat higher than those obtained with XRD (14.4 GPa)^{4,5} or Raman spectroscopy (13.5 GPa).⁶ Raman spectra obtained from the sample studied in this work (not shown) display strong Raman bands of rs-InN at 14 ± 0.5 GPa, in agreement with the previous studies. We conclude that for pressures around the phase transition the optical absorption is dominated by the presence of highly-absorbing domains of w-InN. More importantly, our results rule out the possibility that the presence of GaN/sapphire in our sample delays the phase transition. As for the effect of the sapphire substrate on the pressure coefficients, given the different bulk moduli of InN and sapphire, one could expect some biaxial component

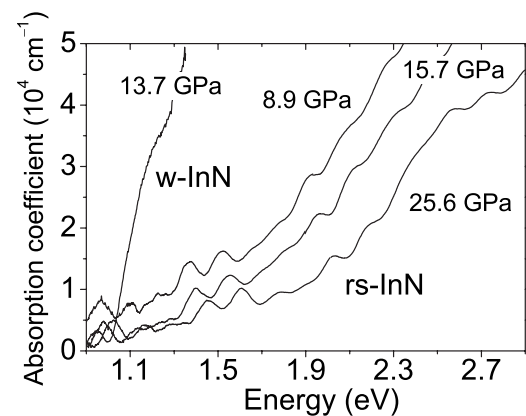


FIG. 3. Optical absorption spectra at 300 K from an InN epilayer obtained at different pressures on the upstroke (curves at 13.7, 15.7, and 25.6 GPa) and on the downstroke (curve at 8.9 GPa).

in the stress tensor acting on the InN film. In the case of our sample, the biaxial components in the stress tensor should be much larger than for the sample studied in Ref. 2, since our InN epilayer is 40 times thinner than the remaining sapphire (the InN film of Ref. 2 was only four times thinner than the substrate). The fact that the pressure coefficients are so close in both cases suggests that the possible effect of biaxial stress is not significant. This, however, does not diminish the obvious interest of additional experiments with free standing thin films or small single crystals.

As can be observed in Fig. 3, the low-energy tail of the absorption spectra of rs-InN exhibits a much less abrupt increase with increasing $h\nu$ in comparison to the spectra of w-InN. The absorption coefficient of rs-InN displays an almost quadratic dependence on $h\nu$, which indicates that rs-InN is an indirect gap semiconductor. Similar observations have been reported in other wurtzite semiconductors like ZnO.²⁰ This finding confirms the results of several *ab initio* calculations for rs-InN based on the linear muffin-tin orbital method¹⁰ and density functional theory (DFT),^{11–13} which predicted indirect band gap values of 1.17 eV (Ref. 10), 1.07–1.87 eV (Ref. 12), and ~ 0.5 eV (Refs. 11 and 13). Unfortunately, the small thickness of our InN epilayer prevents the clear observation of the indirect absorption edge, and as a consequence it is very difficult to accurately determine the indirect band gap energy value of rs-InN with the present measurements. Assuming a $(h\nu - E_g)^2$ dependence for $\alpha(h\nu)$, we estimate that the indirect band gap of rs-InN is 1.0 ± 0.2 eV at 15.7 GPa, in qualitative agreement with most of the calculated band gap values.

The absorption edge of rs-InN clearly shifts to higher energies with increasing pressure (see Fig. 3). A pressure coefficient can be estimated from the shift at constant $\alpha(h\nu)$. For $\alpha(h\nu)$ values between 2×10^4 and 6×10^4 cm⁻¹, the pressure coefficient turns out to be of about 25 ± 5 meV/GPa. Such high $\alpha(h\nu)$ values seem more typical of the onset of an allowed direct transition.²⁰ According to the calculations of Ref. 11 the lowest direct transition in rs-InN is a Γ - Γ transition of 1.5 eV at 15 GPa. Most probably, this value underestimates the actual direct band gap because it is obtained with DFT calculations in the local density approximation (LDA). Here, in order to obtain a corrected value, we reasonably assume that the underestimation of the band gap values within DFT-LDA is the same for the indirect (Σ - Γ and L- Γ) and the direct (Γ - Γ) transitions, since all these transitions share the final state (and ground states are considered to be accurately determined by DFT-LDA methods). Then, comparing the indirect band gap energy values obtained with our measurements (~ 1 eV at 15.7 GPa) to those calculated in Ref. 11 (0.5 eV at the same pressure) we obtain a corrected value for the Γ - Γ direct gap of ~ 2 eV. This value is fully consistent with the onset of intense absorption in the spectra of Fig. 3. Also, the pressure coefficient that we obtain from the absorption measurements is close to that found in Ref. 11 for the Γ - Γ direct transition (30 meV/GPa). On the basis of these results we can reasonably assign the onset of intense absorption in rs-InN to the direct transition of lowest energy (Γ - Γ).

A clear hysteresis effect was observed on the down-stroke. At pressures lower than the transition pressure the absorption curves still displayed the characteristic shape of the indirect absorption edge (see for instance the spectrum at 8.9 GPa of Fig. 3). Similar observations were reported in Refs. 4 and 6. In the present study, we found that for pressures below ~ 4 GPa the rocksalt-to-wurtzite backtransformation occurs. The phase transition is thus fully reversible, although we cannot rule out that some amorphization effect has taken place.

In conclusion, $\alpha(h\nu)$ is enhanced in w-InN well above the absorption edge by the strong nonparabolicity of the energy bands. Rs-InN is an indirect band gap semiconductor with $E_g = 1.0 \pm 0.2$ eV at the phase transition pressure, which is found to be 15.3 ± 0.5 GPa with the optical measurements. Rs-InN exhibits a direct gap (Γ - Γ) around 2.0 eV with a pressure coefficient of 25 ± 5 meV/GPa.

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