We report high-pressure optical absorption measurements on InN epilayers with a range of free-electron concentrations between $5 \times 10^{17}$ and $1.6 \times 10^{19}$ cm$^{-3}$ in order to investigate the effect of free carriers on the pressure coefficient of the optical band-gap of wurtzite InN. With increasing carrier concentration, we observe a decrease of the absolute value of the optical band-gap pressure coefficient of wurtzite InN. Analysis of our data based on the $k \cdot p$ model allows us to obtain a pressure coefficient of 32 meV/GPa for the fundamental band-gap of intrinsic wurtzite InN. Additionally, optical absorption measurements on a 5.7-µm-thick InN epilayer at pressures above the wurtzite-to-rocksalt transition has allowed us to obtain an accurate determination of the indirect band-gap energy of rocksalt InN as a function of pressure. Around the phase transition ($\approx 15$ GPa), a value of 0.7 eV is obtained whose pressure coefficient is around 23 meV/GPa.

I. Introduction

InN and related group-III nitride alloys such as InGaN and InAlN have enormous potential to develop novel applications for optoelectronics, photovoltaics or high-frequency electronics. The revision of the band gap energy of wurtzite-type InN (w-InN) to a value of only $E_g = 0.7$ eV gave rise to renewed interest in these compounds, since their band gap energy may be tuned over a wide spectral range, from the near
infrared to the ultraviolet. This remarkable property could be exploited to fabricate high-efficiency solar cells and light emitting diodes [1].

In spite of much effort to investigate the structural, electronic, optical, and vibrational properties of w-InN at ambient pressure, relatively little is known about the properties of this material as a function of pressure (P). X-ray diffraction (XRD) and Raman scattering studies showed that the wurtzite-to-rocksalt phase transition takes place around 14 GPa [2][3][4][5]. From these structural and lattice-dynamical investigations, values for the bulk modulus and mode Grüneisen parameters of both phases were obtained. In turn, several works have studied the pressure dependence of the fundamental band-gap of wurtzite-type InN and InGaN [6][7][8][9]. In general, it is found that the pressure dependence of the optical-emission peak energy in InN and InxGa1-xN is weaker than that of the absorption edge [6]. The observed differences were attributed to a sizeable contribution of impurity states to the optical emission of the samples. Other authors, however, by direct comparison of PL data with calculated pressure coefficients concluded that the PL emission from wurtzite-type InN and InGaN has mainly band-to-band character [10]. On the other hand, Kamińska et al. [8] showed that conduction-band filling has a clear effect on the photoluminescence (PL) peak pressure coefficient, dEPL/dP, of w-InN. This effect can be attributed to a reduction of the Fermi energy with increasing pressure as a consequence of the increasing electron effective mass. However, with the PL data alone it is not possible to rule out that the experimental dEPL/dP values are further reduced by impurity emission. Bearing in mind the different pressure coefficients measured so far in InN and InGaN with PL and absorption techniques, high-pressure studies of the optical absorption properties of these compounds could provide additional information about the localized/band-to-band character of their PL emission and about the absorption-edge pressure coefficients, dEabs/dP, as a function of the free-carrier concentration (n).

On the other hand, it has been recently shown that rocksalt InN (rs-InN) is an indirect semiconductor with a band gap energy near 1.0 eV at the transition pressure [11]. However, in that work the very low absorbance of the sample investigated (an InN epilayer with a thickness of 500 nm) allowed only the determination of the higher energy direct transition at the Γ point. Therefore, an accurate determination of the energy of the indirect band-gap of rs-InN and its pressure dependence is thus necessary.

In the present work we carry out high-pressure optical absorption measurements in w-InN and rs-InN. We investigate the effect of free carriers on the pressure coefficient of the optical band-gap of w-InN. For this purpose, different samples with carrier concentrations in the 5×10^{17}-1.6×10^{19} cm^{-3} range are employed. Optical measurements on the thickest epilayer available (5.7 µm) allow us to study in detail the wurtzite-to-
rocksalt transition and to obtain an accurate determination of the energy of the indirect band-gap of rs-InN and its pressure behavior.

II. Experiment

Four nominally undoped c-face w-InN epilayers were grown by molecular beam epitaxy (MBE) on sapphire substrates with background electron concentration (thickness) of $5 \times 10^{17}$ cm$^{-3}$ (5.7 µm), $2 \times 10^{18}$ cm$^{-3}$ (500 nm), $6.5 \times 10^{18}$ cm$^{-3}$ (400 nm), and $1.6 \times 10^{19}$ cm$^{-3}$ (400 nm), respectively [12]. Flakes containing InN were detached from the substrates and loaded together with several ruby chips into a 200-µm-diameter hole drilled on a 50-µm thick Inconel gasket. The gasket was placed between the two diamond anvils of a membrane-type diamond anvil cell. Methanol–ethanol–water (16:3:1) was used as pressure-transmitting medium and pressure was determined from the fluorescence of ruby chips [13]. Room-temperature optical absorption of the flakes was measured as a function of pressure by using a microscopic setup using a tungsten lamp, spatial filters, and reflective objectives. For the mid-infrared spectral range, the measurements were performed by using a single-grating monochromator and PbS or InAs detectors with lock-in amplification; while for near-infrared and visible measurements, a multichannel spectrophotometer was employed.

III. Results and discussion

A. Wurtzite InN

Optical absorption measurements were carried out in order to investigate the electron-density dependence of the band-gap pressure coefficients of w-InN. Figure 1 shows the absorption coefficient ($\alpha$) at different pressures for the two w-InN epilayers having low and high electron densities ($n = 5 \times 10^{17}$ cm$^{-3}$ and $1.6 \times 10^{19}$ cm$^{-3}$ in Figs. 1(a) and (b), respectively). Both figures show the expected blueshift of the absorption edge with increasing pressure and the effect of conduction-band filling. The latter is evidenced in Fig. 1 by the higher energy of the absorption edge in the absorption spectra of the lower panel, i.e., in the spectra of the sample with $n = 1.6 \times 10^{19}$ cm$^{-3}$. From an analysis of the absorption coefficient at ambient pressure based on a sigmoidal dependence on photon energy [12], we extract for the sample with $n = 5 \times 10^{17}$ cm$^{-3}$ a band-gap energy value of 0.65 eV. This value is in excellent agreement with that obtained with the same procedure for samples with similar electron densities (0.64 eV, see Ref. [12]). With increasing $n$, we find that the band-gap energy monotonically increases up to $\approx 0.8$ eV for $n = 1.6 \times 10^{19}$ cm$^{-3}$, in very good agreement with published values [13] [14].
Figure 2 shows the pressure coefficient of the absorption edge, $dE_{\text{abs}}/dP$, as a function of $n$, as extracted from the pressure-dependent optical absorption measurements on the different samples studied in this work. Data from Ref. [6], also obtained with optical absorption experiments, have also been included in the plot for comparison. As can be seen in the figure, $dE_{\text{abs}}/dP$ is reduced from 30-32 meV/GPa for the samples with the lowest electron densities down to about 24 meV/GPa for $n = 1.6 \times 10^{19} \text{ cm}^{-3}$. A similar observation was obtained by low-temperature PL measurements in Ref. [8] and attributed to conduction-band filling effects. Data points from this work can also be found in Fig. 2. However, the $dE_{\text{PL}}/dP$ values reported in that work were consistently lower than those obtained with the present optical absorption measurements (for instance, 27.3 meV/GPa at $n = 3.6 \times 10^{17} \text{ cm}^{-3}$ and 20.8 meV/GPa at $n = 1.1 \times 10^{19} \text{ cm}^{-3}$, see Ref. [8]). This observation seems to confirm that the pressure dependence of the PL emission in InN is in general weaker than that of the absorption edges. In Ref. [6] the difference between the pressure coefficients obtained with emission and absorption techniques was related to the possible participation of impurity states (i.e., of highly localized states with low pressure coefficients) in the PL emission of InN.

The solid line in Fig. 2 shows the result of a calculation of the pressure coefficient of the optical band-gap as a function of $n$ in w-InN. This calculation was performed by using an approximation of the two-band $k \cdot p$ Kane model in the small effective mass limit to take into account the non-parabolicity of the conduction band of InN [14]. Following Ref. [8], it was assumed that the pressure coefficient of the optical band-gap ($dE_{\text{abs}}/dP$) has two contributions: one from the band-gap pressure coefficient in the intrinsic semiconductor, $dE_G/dP$, and a second one arising from the pressure dependence of the Fermi energy, $dE_F/dP$. The latter is a consequence of the flattening of the conduction band (i.e., of the increasing electron effective mass) with increasing pressure, and therefore it has a negative value. To calculate the derivative of $E_F$ as a function of $n$ and obtain the curve of Fig. 2, the Fermi energy was numerically calculated for different $n$ and $P$ values at room temperature by taking a zone-center electron effective-mass value equal to $m^* = 0.07 \cdot m_e$ at ambient pressure ($10^{-4}$ GPa) [1]. Pressure-dependent $m^*(P)$ values were obtained by using the expression $m^*(P) = m^*E_G(P)/E_G$ from $k \cdot p$ theory, where $E_G = 0.65$ eV is the band-gap of InN at ambient pressure and $E_G(P)$ is assumed to vary linearly with pressure, i.e., $E_G(P) = E_G + (dE_G/dP)P$, where $dE_G/dP$ is left as an adjustable parameter.

Within this approach, we find that a value of $dE_G/dP = 32$ meV/GPa yields the best agreement between the theoretical and experimental data over a large range of electron densities (see Fig. 2). This pressure coefficient value is in very good agreement with the predictions of many-body perturbation theory in the $G_0W_0$ approximation [15]. Such calculations, which provide excellent $E_G$ values for w-InN at ambient pressure (0.69 eV), yield $dE_G/dP$ values in the range of 28–33 meV/GPa [15].
It should be noted that in the range of low electron densities \( (N_e < 10^{18} \text{ cm}^{-3}) \), where conduction-band-filling effects are expected to be small, the \( dE_{\text{abs}}/dP \) curve calculated by using \( dE_G/dP = 32 \text{ meV/GPa} \) falls between the two data points obtained with optical absorption measurements plotted in Fig. 2 (one of them from Ref. [6]). Note that when \( n \) goes to zero the Fermi energy exhibits some pressure dependence arising from the pressure dependence of \( m^* \) in the intrinsic semiconductor. As a consequence, for low electron densities the calculated \( dE_{\text{abs}}/dP \) values in Fig. 2 do not tend to \( dE_G/dP = 32 \text{ meV/GPa} \) but to a somewhat lower value (=30.5 meV/GPa).

As can be seen in Fig. 2, the reduction of \( dE_{\text{abs}}/dP \) predicted by the \( \mathbf{k} \cdot \mathbf{p} \) calculation agrees well with the experimental data obtained by optical absorption measurements for the samples with higher electron densities, thus confirming that conduction-band filling is responsible for the reduction of \( dE_{\text{abs}}/dP \) with increasing \( n \). Our data and analysis suggest that the true value of \( dE_G/dP \) in intrinsic w-InN is 32 meV/GPa, in the upper limit of the calculations of Ref. [15]. By using the bulk modulus \( (B_0= 125.5 \text{ GPa}) \) obtained from XRD measurements by Ueno et al. [2], we obtain a volume deformation potential for w-InN of \( dE_G/d \ln V = -4.0 \text{ eV} \).

For sufficiently high electron concentrations, band-gap renormalization effects arising from electron-electron interactions and carrier-ion correlations are expected to yield reduced band-gap energies [14]. These many-body effects compensate the magnitude of the band-gap increase arising from conduction-band filling and result in energy redshifts of about 150 meV per decade of change of \( n \) above \( 10^{19} \text{ cm}^{-3} \) in w-InN [14]. Here, in order to evaluate the role of band-gap renormalization on \( dE_{\text{abs}}/dP \), we have calculated the pressure coefficients for the conduction-band shifts resulting from electron-electron interaction \( (\Delta E_{e-e}) \) and electron-ion interaction \( (\Delta E_{e-i}) \) as a function of \( n \). For this purpose, we have used the expressions given in Ref. [14] for both \( \Delta E_{e-e} \) and \( \Delta E_{e-i} \) and we have obtained their pressure derivatives by numerical methods. Below \( 5\times10^{18} \text{ cm}^{-3} \), our calculations yield pressure coefficients for \( \Delta E_{e-e} + \Delta E_{e-i} \) lower than 1 meV/GPa. For electron concentrations close to that of our most heavily doped sample \( (1.6\times10^{19} \text{ cm}^{-3}) \), we find that \( d(\Delta E_{e-e} + \Delta E_{e-i})/dP \sim 2 \text{ meV/GPa} \). Given that this value is still comparable to the experimental error of the pressure-dependent optical measurements, it can be assumed that band-gap renormalization effects play a minor role in the results of Fig. 2. In contrast, in the ultra-heavily doped regime \( (N_e \sim 10^{20} \text{ cm}^{-3}) \), we obtain pressure coefficients for the band-gap renormalization shifts that are higher than 4 meV/GPa. Such values are expected to compensate the reduced \( dE_{\text{abs}}/dP \) values predicted by the \( \mathbf{k} \cdot \mathbf{p} \) calculations for high electron densities (see Fig. 2). Note however that the \( \mathbf{k} \cdot \mathbf{p} \) model is expected to fail in the ultra-heavily-doped range. Additional work would be desirable in order to ascertain the role of conduction-band filling and band-gap renormalization on the high-pressure optical properties of ultra-heavily-doped w-InN.
B. Rocksalt InN

Rocksalt InN is an indirect semiconductor with a band-gap energy that lies around 1 eV [11]. In this work we perform a detailed study of the pressure dependence, up to 30 GPa, of the indirect band-gap of rs-InN using a thick InN epilayer (5.7 µm). Figure 3 shows three different absorption spectra obtained on the upstroke at 12.1, 15.3, and 17.4 GPa for this sample. The wurtzite-to-rocksalt phase transition is clearly observed as a change in the shape of the absorption edge with increasing pressure. At 15.3 GPa, the profile at higher photon-energy values of the spectrum still resembles that of the wurtzite phase. In contrast, from the absorption curve at 17.4 GPa it can be concluded that the phase transition is complete. As discussed in Ref. [11], the wurtzite-to-rocksalt phase transition pressure in InN tends to be higher in optical absorption measurements than those obtained from XRD or Raman scattering measurements. This discrepancy may be attributed to the presence of remaining, highly-absorbing w-InN domains in the flakes around (or just above) the transition pressure.

High-pressure absorption measurements were obtained in the upstroke cycle up to 30 GPa and then in the downstroke cycle down to ambient pressure. Figure 4 shows the absorption spectra of rocksalt InN obtained in the downstroke cycle, from 30 GPa down to 4.4 GPa. The expected redshift of the absorption edge with decreasing pressure is observed. It should be noted that the absorption spectra of rs-InN obtained in the upstroke cycle ($P > 17.4$ GPa) yielded similar profiles and have not been included in the subsequent analysis. The characteristic shape of the indirect absorption edge is observed in the figure down to 4 GPa. Thus, a clear hysteresis effect is observed. As in Ref. [11] for the case of a much thinner epilayer, we find that for $P < 4$ GPa the rocksalt-to-wurtzite backtransformation occurs (not shown).

The quadratic dependence of the low-energy tail of the absorption edge of rs-InN confirms the indirect nature of this semiconductor compound. In Fig. 5 we have plotted the square root of the absorption coefficient of rs-InN for two different pressure values (downstroke cycle). In both cases, a clear linear dependence arising from an indirect transition is observed. For a pressure of 13.4 GPa, close to the pressure at which the wurtzite-to-rocksalt transformation occurs, the low-energy tail can be assigned to an indirect band-gap with an energy of $0.70 ± 0.05$ eV. This value is lower than that previously measured in thinner epilayers (1 eV at 15.7 GPa, see Ref. [11]). While in Ref. [11] the small thickness of the sample prevented the clear observation of the indirect absorption edge, since the transmittance was dominated by the allowed higher-energy direct transition at the $\Gamma$ point, the present measurements provide a much more accurate determination of the indirect band-gap energy of rs-InN.
Previous theoretical works predicted a broad range of possible indirect band-gap values for rs-InN [16][17][18][19], ranging from 0.5 eV [17][19] up to 1.9 eV [16]. The present measurements indicate that the indirect band-gap energy of rs-InN lies in the lower range of the theoretical calculations, i.e., in agreement with the results of Refs. [17] and [19]. These two works predict that the lowest band-gap of rs-InN corresponds to a L–Γ transition.

From the spectra of Fig. 4, a pressure coefficient for the indirect band-gap of rs-InN can be estimated from the shifts at constant absorption coefficient. We show in Fig. 6 the pressure dependence of the energy shift of the absorption edge at three different values: 1100, 1500 and 2000 cm\(^{-1}\). A pressure coefficient of 23 meV/GPa is extracted from a linear fit to the data of Fig. 6. This value, slightly lower than that of the direct band-gap in the wurtzite phase (32 meV/GPa), allows us to obtain the volume deformation potential for the indirect transition in rs-InN. By using the bulk modulus of rs-InN \((B_0 = 170 \text{ GPa}) [3]\) we obtain a value of \(\frac{dE_G}{d\ln V} = -3.9 \text{ eV}\), only slightly below the deformation potential of the direct fundamental band-gap of w-InN.

IV. Conclusion

Conduction-band filling yields reduced optical band-gap pressure coefficients in w-InN with increasing carrier concentration. The experimental pressure coefficients in w-InN, measured with optical absorption experiments, are found to be higher than those obtained by PL measurements in previous works. A \(k\cdot p\) calculation allows us to reproduce the weakening of the experimentally-determined band-gap pressure coefficients with increasing electron density. We conclude that the best value for the band-gap pressure coefficient in intrinsic w-InN is 32 meV/GPa. The wurtzite-to-rocksalt phase transformation is observed around 15 GPa. Around the transition pressure, a band-gap of 0.7 eV is obtained for the rocksalt phase. From the high-pressure optical measurements, the pressure coefficient for the indirect band-gap of rs-InN is obtained: 23 meV/GPa.

References


FIGURES

Figure 1: Optical absorption spectra at different hydrostatic pressures of two different InN epilayers with free-electron concentration of (a) $5 \times 10^{17}$ cm$^{-3}$ (thickness 5.7 µm) and (b) $1.6 \times 10^{19}$ cm$^{-3}$ (thickness 5.7 µm).

Figure 2: Pressure coefficient of the optical band-gap of InN as a function of electron concentration. The data obtained in this work with high-pressure optical absorption measurements are plotted with circles. Data reported in Refs. 6 (triangle) and 8 (squares), obtained with optical absorption and PL measurements, respectively, have also been included in the plot. The curve is the calculated dependence based on the $k \cdot p$ model. For the calculation, a band-gap pressure coefficient of 32 meV/GPa at zero electron concentration has been used.

Figure 3: Optical absorption spectra at different hydrostatic pressures around the wurtzite-to-rocksalt transition of a 5.7-µm thick InN epilayer with free-electron concentration of $5 \times 10^{17}$ cm$^{-3}$.

Figure 4: Optical absorption spectra at different hydrostatic pressures (downstroke cycle) of rs-InN. Measurements were performed on a 5.7-µm thick InN epilayer with free-electron concentration of $5 \times 10^{17}$ cm$^{-3}$.

Figure 5: Square root of the room-temperature absorption coefficient of rs-InN measured at two different hydrostatic pressure values. From a linear fit to the data, energy values for the indirect band-gaps are evaluated.

Figure 6: Pressure dependence of the absorption edge of rs-InN at three different (constant) absorption-coefficient values. A linear fit to the data allows us to evaluate the pressure coefficient of the indirect band-gap of rs-InN.
Figure 1

Figure 2
Figure 5

Figure 6