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Fundamental energy gap of GaN from photoluminescence excitation spectra

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In the absence of samples suitable for transmission measurements, photoluminescence excitation spectra (PLE) have been found useful in the evaluation of detailed information about the lowest direct-absorption edge of GaN. In this work the results of PLE measurements are combined with data on reflection and luminescence in the intrinsic region to determine the positions of A-, B-, and C-exciton ground-state transition energies and the lowest band gap. Neglecting polariton effects, the value of the A-exciton ground-state transition energy is determined as being $E_A^x = 3.4751 \pm 0.0005$ eV at 1.6 K from combined PLE and emission spectra. The corresponding values for B and C exciton transitions are found to be $E_B^x = 3.4815 \pm 0.001$ eV and $E_C^x = 3.493 \pm 0.005$ eV from PLE spectra. The lowest band gap is determined to be $E_g^A = 3.503^{+0.005}_{-0.002}$ eV at 1.6 K, which fixes the ground-state A-exciton binding energy as $E_B(A) = 28^{+6}_{-3}$ meV, in good agreement with the effective-mass value. The temperature dependence of the band gap could also be accurately measured in PLE spectra and can be described by an expression $E_g^A = [3.503 + (5.08 \times 10^{-4} T^2)/(T - 996)]$ eV for $T < 295$ K, with an estimated relative uncertainty of ± 0.002 eV.

I. INTRODUCTION

GaN is large-band-gap semiconductor with wurtzite structure, contrary to most other (cubic) group-III-V compounds. The lowest fundamental energy gap of GaN has previously been shown to be direct, situated at the Γ point with a value of about 3.50 eV at low temperatures.[1,2] From observations of exciton-reflection spectra for three configurations of polarization and propagation vector relative to the crystal axis, it has been established that the split-valence band has the normal order; i.e., Γ_9^v is the upper one, as in CdS.[1] From these measurements, the excitonic transition energies at low temperature could also be established to within a few meV. More detailed information would be obtained most directly by measurements of the absorption coefficient over the entire edge region, which is very hard to do experimentally. Good quality single-crystalline epitaxial layers on sapphire presently appear to require a thickness of at least 100 μ, and no technique is at present available giving samples suitable for transmission measurements (this involves removing the entire substrate and the GaN layer except for the uppermost $\sim 1 \mu$). Although adequately thin single crystals can be prepared by vapor transport[3] and used as grown, the carrier concentration in these small crystals is at present far too high to permit accurate estimation of details in the absorption-edge characteristic for pure crystals.

There is, however, another method of obtaining information about the structure of the absorption edge, namely by measurement of photoluminescence excitation spectra (PLE). In this method, crystals of arbitrary thickness and geometry can be used, and accurate results for absorption-edge structures have previously been obtained for both indirect and direct fundamental transitions in other group-III-V compounds.[4,5] In this paper, results from PLE measurements are reported for GaN at temperatures below 300 K. At low temperatures, exciton series connected with all three valence subbands are observed, together with an additional rise near the band gap. The identification of these transitions could be made by comparison with reflection spectra. The lowest-energy free-exciton transition can also be observed in luminescence at somewhat elevated temperatures (> 30 K), which gives a more accurate determination of its transition energy. Since the "C"-exciton transition in PLE spectra, together with the rise near the band gap could be followed up to room temperature, an accurate determination of the temperature dependence of the band gap for GaN could be obtained for the first time. It appears that this temperature dependence is much less than most previous estimations.[6–8]

II. MATERIALS AND EXPERIMENTAL PROCEDURE

The GaN crystals used in this investigation were grown by vapor-phase epitaxy on sapphire employing a technique similar to the one previously reported.[9] The growth temperature was kept at 1025-1050 °C in a single-zone furnace; typical values for gas flow rates being the following: HCl (99.995%) 0.2 liter/min, N_2 (99.9995%, carrier gas) 1.2 liter/min, and NH_3 (99.999%) 1.4 liter/min. Ga (99.9999$^+$%) was introduced in a quartz boat at about 900 °C upstream from the growth zone in the furnace. Growth rates in excess of 5 μm/min could be obtained for the (0001)-oriented single-crystalline layers. However, the most favorable rate was found to be about 1 μm/min for good crystal quality. For these experiments we used layers lightly doped with Cd, the room-temperature free-carrier concentration being reduced to below 10^{18} cm^{-3} in good layers (thickness >100 μ), as deduced from electrical measurements.[10] These layers were uncolored as were the undoped layers, but the advantage of Cd doping (besides a slight reduction in free-carrier concentration) was a strong blue emission band peaking at 2.7 eV[10] which could easily be isolated for PLE measurements.

Optical spectra were obtained at low temperatures with crystals immersed in liquid (or cooled gaseous) He or N_2. PLE spectra and reflection spectra were obtained with a 250-W tungsten-halogen lamp as light source together with a Jarrel Ash 25-104 double-Czerny-Turner monochromator. A cooled EMI 9659 photomultiplier was used as a detector for photoelectric recording. In PLE spectra the exciting radiation was blocked by placing suitable glass filters between the cryostat and the detector, so that only photons with energy < 3.0 eV could reach the detector. PLE spectra were normally taken employing a 90° angle between exciting and emitted radiation, i.e., the emission was detected at an angle of 45° to the *c* axis (which is perpendicular to the crystal surface). In this geometry, transitions involving all three valence subbands are observable. Reflection spectra were obtained only on a relative scale, and in the α mode ($\vec{E} \perp \vec{c}$, $\vec{k} \parallel \vec{c}$). Although the angle of incidence was sometimes as large as (4–5)°, this should not cause any measurable deviation from a pure $\vec{E} \perp \vec{c}$ spectrum, judged from previous investigations on CdS.[11] Finally, luminescence measurements were obtained employing a 100-W mercury lamp as a (rather low-intensity) excitation source. Rather high-photon enerfies (around 4 eV) were selected to minimize distortion of emission spectra via self-absorption.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

A. Interpretation of PLE spectra and comparison with reflection data

In Fig. 1 is shown the typical behavior of PLE spectra from a slightly Cd doped 110-μ-thick GaN epitaxial layer at 1.6, 77, and 295 K. At low temperatures, a well-defined structure is observed reflecting the corresponding behavior of the absorption edge, where three different discrete *A*-, *B*-, and *C*-exciton ground-state peaks are expected below the absorption rise near the band gap. In principle, peaks in the absorption coefficient might give rise to either *peaks* or *dips* in the PLE spectra, depending on the strength of the (nonradiative) surface recombination.[4,5] Comparison with reflection spectra of the same crystal at 1.6 K (Fig. 2) shows, however, that the peaks in PLE spectra are associated with peaks in these reflection spectra, which in turn are associated with peaks in the absorption spectrum.[11] The reflection spectrum in Fig. 2 is in excellent agreement with the corresponding α mode ($\vec{E} \perp \vec{c}$, $\vec{k} \parallel \vec{c}$) spectrum published by Dingle *et al.* for undoped material.[1]

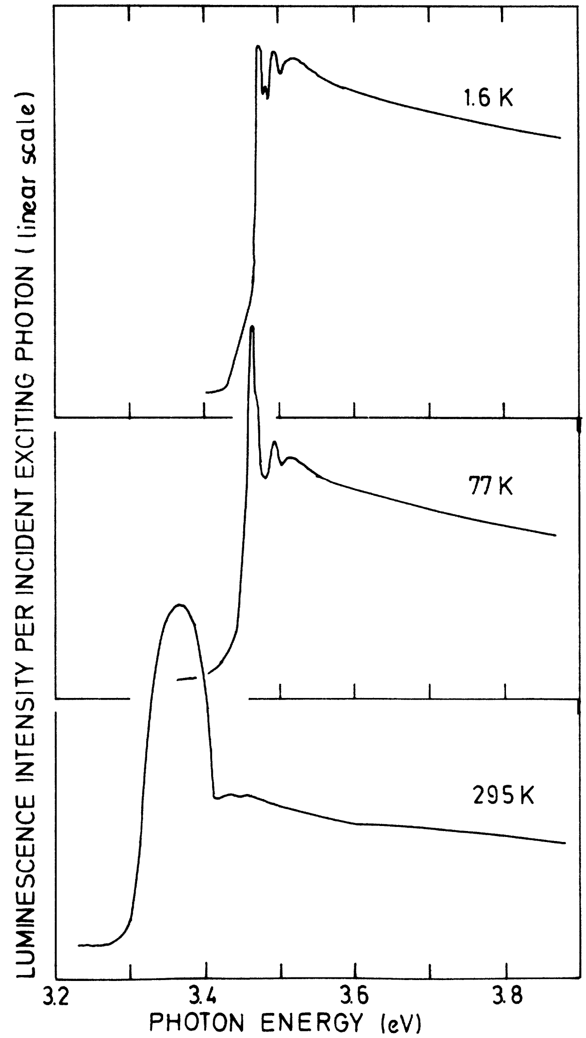

FIG. 1. PLE spectra of blue 2.7-eV emission from a 110-μ-thick slightly Cd doped GaN single-crystalline epitaxial layer at three different temperatures. (All PLE spectra shown in this work are corrected to constant photon flux at each exciting photon energy, which can easily be done since the blue emission varies linearly with excitation intensity.) Note that the *C* emission line together with the rise at the band gap at ~10 meV higher energy is observable even at 295 K. The broad peak observed at 3.365 eV at 295 K is not directly related to the lowest *A*-exciton line (see text).

The low-energy peak with maximum at about 3.472 eV in PLE spectra at 1.6 K is due to absorption in both bound-exciton (at 3.469 eV[10]) and free-exciton states (the Γ_9^v-Γ_7^c A line). This peak exhibits a strong broadening and shift into the extrinsic region between 100 and 295 K, and at 295 K the broad peak has its maximum at about 3.365 eV, about 40 meV below the exciton peak in emission for the same crystal at these temperatures.[10] Considering this large energy shift, and also the fact that this peak in PLE spectra is about a factor of 2 broader than the excitonic edge emission, we believe that the major part of this peak above 100 K is not related to a corresponding excitonic absorption peak.[12]

Disregarding the anomalous behavior of the broad peak, the features observed at higher energies (above 3.475 eV) are independent of temperature, apart from the band-gap shift and thermal broadening of the peaks. The second peak at 3.4815 ± 0.001 eV at 4 K is attributed to the Γ_7^v-Γ_7^c B-exciton ground-state transition in agreement with Dingle *et al.*,[1] since its strength is smaller than both the A and C series lines. The third peak at about 3.493 eV at 1.6 K (Fig. 2) should correspond to the Γ_7^v-Γ_7^c C-exciton transition. This peak is remarkably broadened in PLE spectra as well as in reflection spectra, which makes the assignment of an accurate energy value for this transition impossible. (A corresponding broadening of the C-exciton peak compared with A and B excitons has been observed in absorption measurements on CdS.[13])

For A and B excitons the peaks in the α-mode reflection spectra appear at 1–2 meV lower energy than the corresponding peaks in PLE spectra, but the C-exciton reflection-spectra peaks at 3.488 eV (5 meV below the PLE C peak) and exhibits a broad shoulder at 3.494 eV (Fig. 2). These observations in reflection spectra appear to be in excellent agreement with the results reported in Ref. 1 for α polarization. The discrepancies in peak energies between our PLE spectra and reflection spectra are of the order generally observed in material of similar purity. Details in these reflection spectra cannot be clearly understood until more perfect crystals with a smaller natural linewidth for the excitonic transitions can be prepared. Severe broadening of reflection spectra occurred at higher temperatures, and above 200 K only PLE spectra were suitable for accurate determination of transition energies.

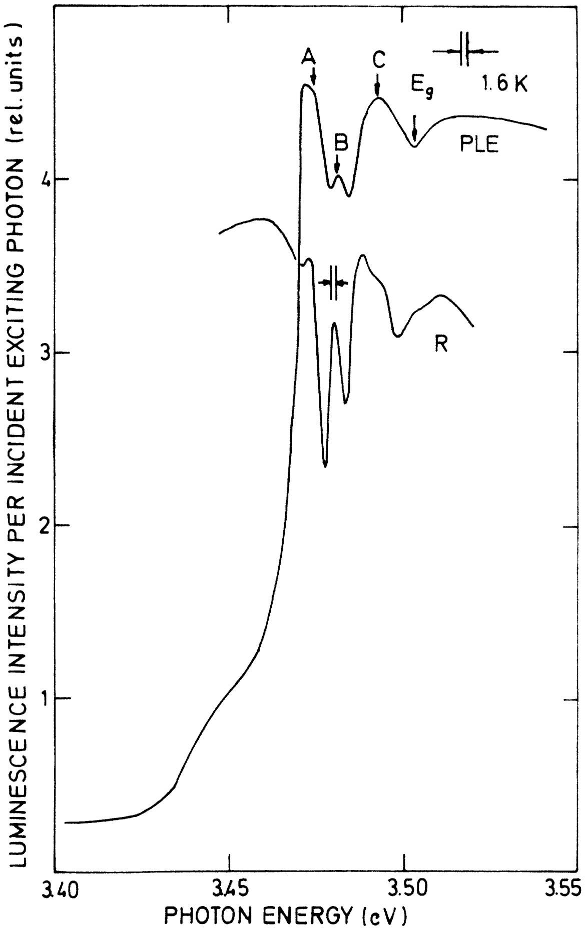

FIG. 2. More detailed view of PLE spectrum from the same crystal as in Fig. 4 at 1.6 K (upper curve) and reflectance curve from the same crystal at 1.6 K shown as comparison (marked R). (The vertical scale refers to the PLE spectrum; the reflectance curve was only measured on a relative scale not shown in the figure.) The PLE spectrum clearly shows peaks corresponding to absorption into both A- (disturbed by bound excitons), B-, and C-exciton ground states, and a rise at higher energy due to intrinsic absorption into continuum states.

The monotonic rise in absorption coefficient starting near the lowest (Γ_9^v-Γ_7^c) band gap is also reflected by a rise in the PLE spectra just above 3.50 eV at 1.6 K, followed by a saturation at about 3.52 eV, and then a slow decrease towards higher-photon energies. This is the expected behavior of a PLE spectrum in the intrinsic region subject to nonradiative surface recombination, when selective excitation effects are not important.[4,5]

A detailed evaluation of the position of the lowest (Γ_9^v-Γ_7^c) band gap from these PLE spectra is influenced by the presence of quasicontinuum absorption from excited bound states of the corresponding free exciton.[14] We may assume that the $n = 2$ excited state contributes to the high-energy side of the broad asymmetric C line (Fig. 2), and a quasicontinuum involving excited states with $n \geq 3$ would then add an uncertainty of about 3 meV to the upper bound of the Γ_9^v-Γ_7^c band gap. Thus the dip between the broadened C-exciton peak and the following absorption rise (Fig. 2) should permit an estimate of this band gap as $E_g^A = 3.503^{+0.005}_{-0.002}$ eV at 1.6 K. This is the first experimental observation of the band

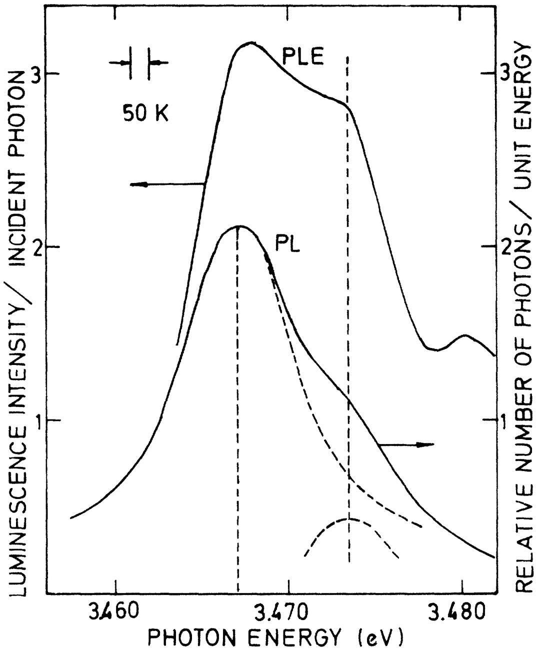

FIG. 3. Comparison between PLE spectrum (upper curve, left-hand scale) and emission spectrum (lower curve, right-hand scale) from the same GaN crystal as in Figs. 1 and 2 at 50 K. The luminescence was excited by photons of about 4 eV and therefore any spectral distortion due to self-absorption effects should be small. The free-exciton line shape in emission is obtained by subtraction of the bound-exciton line, assuming the latter to be symmetrical.

gap of GaN reported and the value agrees well with previous predictions.[1,2]

B. Accurate determination of *A* exciton energy from PLE spectra and luminescence spectra

The determination of the *A*-exciton ground-state transition energy from PLE spectra at lowest temperatures suffers from the difficulty that bound excitons also contribute to the spectrum, as pointed out in Sec. IIIA. At temperatures above 100 K, the lowest-energy peak is also grossly distorted by extrinsic effects (see above). But in the region 30-100 K it is generally possible to observe the *A*-exciton peak as a separate contribution to the high-energy edge of the 3.47-eV peak in PLE spectra (Fig. 3). Since these excitation spectra are expected to be somewhat distorted by variations in the active volume excited, and by the influence of surface recombination with changes in the absorption coefficient, the shape of different overlapping peaks cannot generally be predicted. Thus, more accurate determinations of the exciton-peak position would be obtained from luminescence, since in this case negligible distortion of the emission spectrum can be obtained with optical excitation employing light energies well above the band gap. The observation of the corresponding "emission shoulder" for the *A* exciton is also possible in the temperature interval mentioned ($T > 30$ K). At low temperatures (1.6 K), the peak at 3.469 eV, which in analogy with CdS is believed to be caused by an exciton bound to a neutral donor,[1,10] is found to be symmetrical to a good approximation, and therefore it can be assumed that at 50 K (where this emission has dropped by about a factor of 40 in intensity) its emission shape above intensities of 20% of the peak value should also be symmetrical and can be reproduced by drawing the mirror image of the low-energy edge (Fig. 3). In this way the *A*-exciton line can be separated, and the resulting symmetrical look of this line gives confidence in the procedure adopted.[15] The resulting peak value at 50 K is 3.4735 ± 0.0002 eV and agrees well with the *A* peak observed in PLE spectra at 50 K (Fig. 3). From the separation of the peaks in Fig. 3 an accurate value for the binding energy for the exciton to the donor can also be obtained, $E_{dx} = 6.4 \pm 0.4$ meV. From the shift in the bound-exciton emission-peak position between 50 K and 1.6 K, which was found as 0.0016 ± 0.0003 eV (Fig. 4), the resulting value for the *A*-exciton transition at 1.6 K is 3.4751 ± 0.0005 eV, which is a more accurate value than the previous one, 3.474 ± 0.002 eV obtained from reflection spectra.[1] (The relevance of such an accurate determination can only be settled when the expected effects of spatial dispersion on this *A*-exciton emission can be studied in more

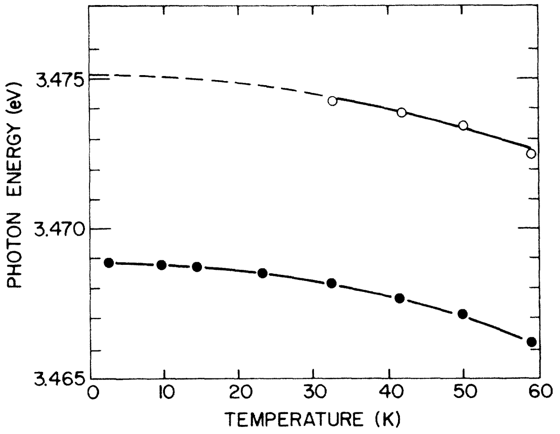

FIG. 4. Illustration of the extrapolation procedure employed to obtain an accurate determination of the *A*-exciton emission peak position (○) at 4 K. The peak position of the dominant bound-exciton emission (●) could be measured accurately in the whole temperature region. The position of the *A* exciton at 4 K is obtained, as indicated in the figure, assuming a temperature-independent binding energy of the exciton to the donor.

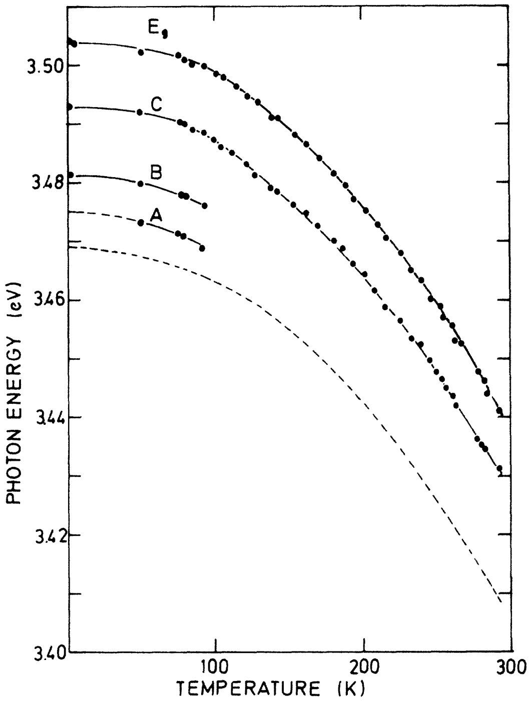

FIG. 5. Temperature dependence of the band gap of GaN and the C-exciton line as deduced from PLE spectra similar to those shown in Fig. 1. A- and B-exciton lines could not be accurately followed above 100 K. The dashed curve is the main excitonic photoluminescence peak as observed in good crystals (Ref. 10).

perfect crystals.[16]) The experimentally determined value for the free-exciton binding energy is thus 28^{+6}_{-3} meV, which is identical to the effective-mass value (about 30 meV) within the present uncertainty of the hole effective mass in GaN.[1,2,17]

C. Temperature dependence of band gap

Since the broad C line (and the rise near the band gap) in the PLE spectra (Figs. 1 and 2) persist up to room temperature, this gives a reliable way of determining the temperature dependence of the band gap of GaN. The C peak does not exhibit any severe broadening below 295 K (since it is already broad at 1.6 K) and its peak position could be found to within 0.002 eV at all temperatures below 295 K, together with the dip defining the band-gap position, which has a distance of 10 ± 2 meV from the C line in the whole temperature region. The resulting temperature dependence is shown in Fig. 5 and is thus believed to be accurate to within 0.002 eV, at least on a relative scale. The structure observed in reflection spectra (Fig. 2) could also be followed up to above 200 K, but the scattering in values from these measurements were considerably larger; and thus these reflection spectra offer a less-accurate method for the determination of the temperature dependence of the absorption edge. From Fig. 5 it is seen that the gap of GaN varies from $3.503^{+0.005}_{-0.002}$ eV at 4 K to $3.440^{+0.005}_{-0.002}$ eV at 295 K, the shift between these temperatures being 63 ± 2 meV. This temperature dependence is considerably smaller than has been reported earlier from different transmission experiments[7,8] or from luminescence data.[6] These earlier transmission measurements were made at the low-energy edge of the A-exciton absorption line well below the peak, and are thus affected by the broadening effects on excitonic edges which at least in impure samples may be strongly temperature dependent. The relative change in band gap between 1.6 and 295 K is larger than our value by 70% in Ref. 7 and 55% in Ref. 8. The band-gap variation deduced from earlier luminescence measurements[6] appear to deviate by more than a factor of 2 from our value. From Fig. 5 it is apparent that any fit of the temperature dependence to a linear relationship below 300 K, as was previously attempted,[6-8] is inadequate. A nonlinear behavior below 300 K for GaN might well be expected for GaN in view of its expected high Debye temperature.[18,19] An empirical fit of Varshni's formula,[18]

$$E_g = E_0 - \alpha T^2/(T+\beta) ,$$

can be made and the resulting numerical expression is

$$E_g^A = [3.503 + (5.08 \times 10^{-4} T^2)/(T - 996)] \text{ eV} ,$$

which is an adequate description of our experimental data for $T < 295$ K within the stated relative uncertainty (2 meV). The constant β in Varshni's formula should correspond to the Debye temperature Θ_D, which can be estimated to be about 600 K in GaN.[20] Since β comes out negative (as for diamond and SiC[18]), no physical meaning can be ascribed to this relation for GaN. (Good agreement with experiments for the above formula with $\beta \approx \Theta_D$ has, however, been obtained for GaAs and GaP from measurement over a larger temperature range.[21]) A significant theoretical calculation of this temperature dependence cannot be made at present, since the parameters involved in the electron-phonon interaction (Debye-Waller factors, etc.) are not experimentally known for GaN. Theoretical estimations of these parameters are not sufficiently accurate as judged from calculations for other group-III-V compounds.[19]

IV. CONCLUSIONS

Photoluminescence excitation spectra (PLE) are shown to be very useful in the study of intrinsic structure at the fundamental absorption edge of GaN. The A-, B-, and C-exciton series are directly observed as peaks in PLE spectra below the rise due to the onset of the lowest direct band-to-band transitions. This interpretation of PLE spectra is confirmed by comparison with reflectance measurements on the same crystals. Neglecting polariton effects, an accurate value for the *A*-exciton ground-state transition energy of $E_A^x = 3.4751 \pm 0.0005$ eV at 1.6 K is obtained from the combined observation of this transition in PLE spectra and in emission spectra above 30 K. The transition energy for the *B*-exciton ground state is found to be $E_B^x = 3.4815 \pm 0.001$ eV at 1.6 K from PLE spectra as well as in reflection spectra, and therefore the determination of its transition energy $E_C^x = 3.493 \pm 0.005$ eV is considerably more uncertain. The dip observed between the *C*-exciton peak and the rise near the lowest Γ_9^v-Γ_7^c band gap is used as a measure of the height of this band gap, and the value observed at 1.6 K is $E_g^A = 3.503^{+0.005}_{-0.002}$ eV, the first experimental observation of this quantity. Thus, the *A*-exciton ground-state binding energy is experimentally found to be 28^{+6}_{-3} meV, in excellent agreement with the theoretical effective-mass value. The temperature dependence of the band gap of GaN below 295 K could be measured accurately for the first time with the PLE method, since both the *C*-exciton line and the rise near the band gap were clearly observable up to 295 K. The band-gap energy E_g as a function of temperature can for practical purposes be approximated as

$$E_g^A = [3.503 + (5.08 \times 10^{-4} T^2)/(T - 996)] \text{ eV} ,$$

for $T < 295$ K, with an estimated relative uncertainty of ±0.002 eV.

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[13] See, e.g., E. Gutsche and J. Voigt, in II-VI-*Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 337.

[14] See, e.g. E. J. Johnson, in *Semiconductors and Semimetals*, edited by R. K. Willardsson and A. C. Beer (Academic, New York, 1967), Vol. 3, pp. 213–217. For the case of an applied magnetic field experimental results are available by E. J. Johnson [Phys. Rev. Lett. 19, 352 (1967)].

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