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Absorption, Reflectance, and Luminescence of GaN Single Crystals

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Analysis of the low-temperature absorption, reflectance, and emission spectra of oriented single crystals of hexagonal GaN demonstrates that the features found at 3.62 eV ($E \perp C$) and 3.72 eV($E \parallel C$) are due to the formation of free excitons associated with a direct energy gap. A close analogy exists between these results and similar data from ZnO, consistent with the relative position of Zn and Ga, and O and N atoms in the Periodic Table. Luminescence spectra present good, although not conclusive, evidence for the hypothesis that this direct gap is also the fundamental energy gap in GaN.

Gallium nitride is a hexagonal III-V semiconductor of contemporary interest. Recent experimental attempts to determine the magnitude and nature of the fundamental energy gap have been made with epitaxial films (< 7000 Å)[1] and layers (≤ 150 μ).[2] The conclusions reached in these investigations are in conflict. Kosicki, Powell, and Burgiel[1] suggest $E_g \sim 3.8$ eV at room temperature, whereas Maruska and Tietjen[2] report $E_g = 3.39$ eV. Both groups believe their absorption measurements indicate a direct fundamental energy gap. The only recently published theoretical estimate of the band structure[3] places the direct gap $\Gamma \rightarrow \Gamma$ at 4.80 eV with an indirect gap $\Gamma - X$ at 6.39 eV.

In this paper we report absorption, reflection, and luminescence data taken on *single*-crystal samples between 300 and 2 °K. These data supplement, and in some cases correct earlier estimates, and we believe they allow the best available analysis of the band edge in GaN.

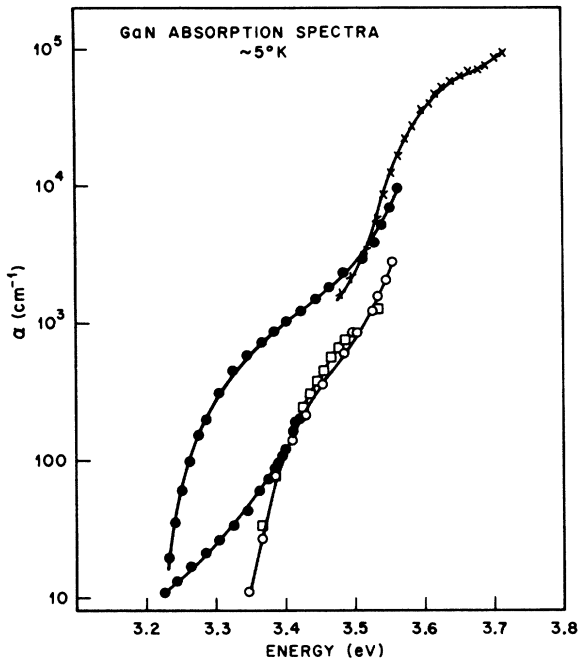

FIG. 1. Axial absorption spectra of GaN platelets at low temperature. The variable absorption for $\alpha \lesssim 1000$ cm^{-1} is extrinsic in origin.

Single-crystal platelets, with the crystal c axis normal to the plate, and hexagonal rods, with the c axis parallel to the rod axis, were grown by Zetterstrom.[4] X-ray measurements confirm the identity of the crystals. Electrical measurements revealed that the crystals were highly n-type with $n \sim 10^{19}/cm^3$. The color of the crystals from any particular growth varied considerably. The measurements to be reported here are only representative of the colorless crystals.

Absorption measurements were made on platelets only (thus given an axial spectrum which, in the case of electric dipole transitions, corresponds to the transverse $E \perp C$ spectrum). The important features of the absorption measurement spectra in Fig. 1 are (i) $\alpha \sim 10^5$ cm^{-1} at about 3.7 eV, (ii) a well-developed shoulder appears at 3.65 eV (at ~5 °K) in the thinnest sample (thickness ~1 μ), and (iii) the absorption edge moves ~0.05 eV to higher energy as the crystal is cooled from room temperature to ~5 °K. The absorption data below $\sim 1.5 \times 10^4$ cm^{-1} in Fig. 1 are consistent with those of Maruska and Tietjen.[2] Their estimate $E_g = 3.39$ eV was obtained from an extrapolated threshold of the low-level absorption and disregards the exciton effects emphasized in this paper. Exciton effects are expected to be very important for direct transitions in a relatively ionic material like GaN.[5] Meaningful $E \parallel C$ absorption measurements could not be obtained from the hexagonal rods because α is too large in the region of interest.

The reflectivity of small plates and rods, which

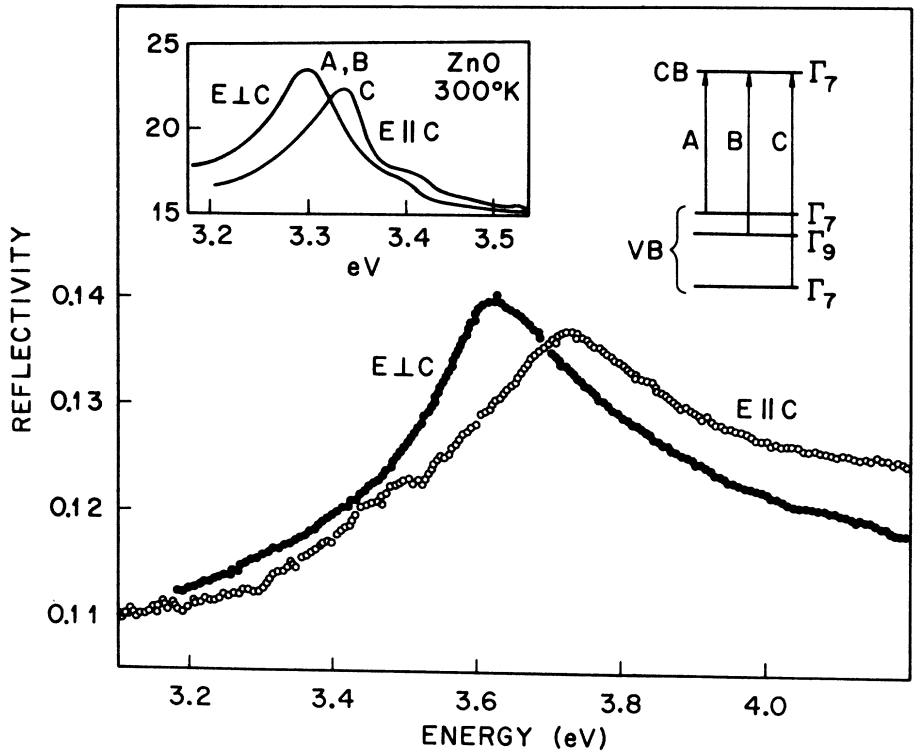

FIG. 2. Reflectance spectra of GaN single crystal at 2 °K. Exciton energy level scheme shown is that used in the analysis of the data, although the present experiments do not resolve the A, B transitions (see text). The insert shows reflectance data for ZnO at 300 °K (after Ref. 9).

had areas in the vicinity of 0.25–1.0 mm^2, was investigated in the range 300–2 °K using the double-beam spectrophotometer recently described by Sell.[6] In Fig. 2 we display $E \parallel C$ and $E \perp C$ spectra taken at 2 °K over the important 3–4-eV range.[7] The energy of the broadened peak at 3.62 eV ($E \perp C$) is in good agreement with the position of the shoulder seen in the $E \perp C$ absorption spectrum of the thin plates, and we attribute both features to the same electronic process. The 3.72-eV peak in the $E \parallel C$ reflectance spectrum should have no equivalent in the $E \perp C$ absorption spectrum. At room temperature the peak positions are 3.57 eV ($E \perp C$) and 3.67 eV ($E \parallel C$). The reflectance measurements were extended to 5.2 eV without disclosing any further structure. From the value of α, $d\alpha/dE$, and the appearance of structure in the reflectance spectra, we propose that the structure is due to strongly broadened exciton transitions at a direct energy gap. We estimate the magnitude of this direct gap to be close to 3.65 eV (2 °K).[8]

It is well-known[9] that the p-like valence band in a wurtzite lattice is split by the combined action of the crystal field (CF) and spin-orbit coupling into three twofold-degenerate (spin included) representations Γ_7, Γ_7, and Γ_9 at $k = 0$. The conduction band is twofold degenerate and transforms like Γ_7. Free excitons may be described by the same symmetry representations as these band-edge states. The band-edge features in both the absorption and the reflection data are attributed to the creation of free excitons in their s-like ground states. By symmetry alone, three transitions are expected (Fig. 2):

$$A: \Gamma_7^{(1)vb} \rightarrow \Gamma_7^{cb}, \quad E \parallel C, \quad E \perp C$$

$$B: \Gamma_9^{vb} \rightarrow \Gamma_7^{cb}, \quad E \perp C$$

$$C: \Gamma_7^{(2)vb} \rightarrow \Gamma_7^{cb}, \quad E \parallel C, \quad E \perp C .$$

The relative intensities, polarizations, and energy splittings depend strongly upon the magnitude of the CF and the spin-orbit coupling.

In the present case, the best approach seems to be to make a direct comparison between our GaN data and similar reflectivity results[9] obtained with the closely related material, hexagonal ZnO. The thermal broadening of this structure is comparable in magnitude to the broadening, presumably due to interactions with the electron plasma, found in our GaN spectra. ZnO was chosen for the comparison not only because it crystallizes in the wurtzite structure, but also because the anions oxygen and nitrogen are adjacent in the periodic table. Thus it is very reasonable to expect that spin-orbit effects on the valence bands of ZnO and GaN will be similar, since the anion should make dominating contributions to the valence-band wave functions. The ordering of the spin-orbit split A, B pair in ZnO ($A < B$) is not expected to be duplicated in GaN since the Zn d orbitals, which are claimed to be responsible for this AB ordering in ZnO, should be considerably closer to the valence band than the corresponding Ga orbitals in GaN. Nevertheless, the above analogy should still be valid since the over-all spin-orbital effects are still expected to be very small.

Thomas,[9] and Liang and Yoffe[10] have shown, in two elegant experimental results, that spin-orbit coupling influences are very small in ZnO (the A, B pair are split by only 4 meV). The similarity between the spectra shown in Fig. 2 lends credibility to the suggestion that spin-orbit effects are similarly small in GaN. Thomas, and Liang and Yoffe have analyzed their low-temperature results with the quasicubic model proposed by Hopfield.[11] When spin-orbit coupling is very weak, the A, B transitions are almost degenerate and essentially $E \perp C$ polarized. The C transition is of similar intensity, but is polarized $E \parallel C$. In ZnO, the energy separation between the (A, B) and the C peaks gives a very good estimate of the size of the CF splitting (~ + 0.04 eV).

Applying the same treatment to GaN, we find that the CF splitting has the same sign, but is considerably larger (~ + 0.10 eV) than in ZnO. We are therefore led to the exciton scheme in Fig. 2 as an

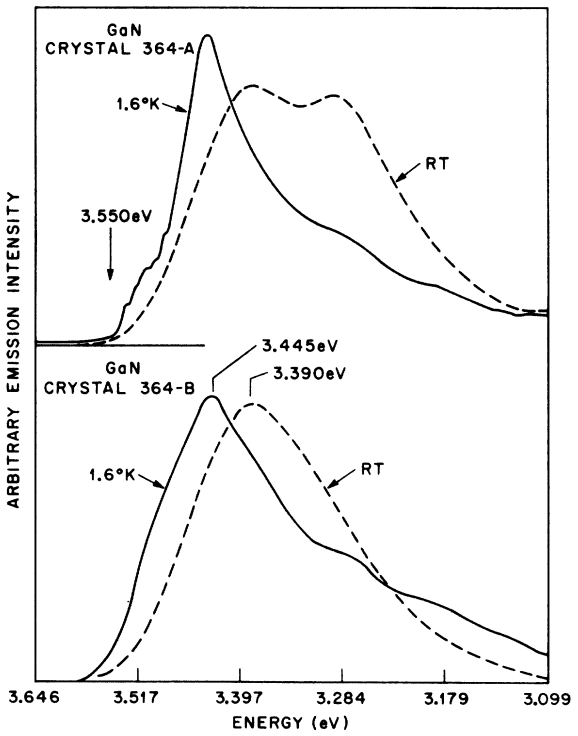

FIG. 3. Typical, N_2-laser-excited luminescence spectra of GaN needles at 300 and 2 °K. The shift of the high-energy peak with temperature is discussed in the text.

interpretation of our optical data. In view of the nature of the data, which presumably will not improve until a major advance in crystal preparation occurs, we do not feel compelled to attempt any more refined analysis at this time.

Is the direct gap, described in the above experiments, the fundamental energy gap of GaN? Because the absorption data in the region below 3.4 eV are difficult to evaluate, no firm answer to this question can be had from the above results. One feature, the variability of absorption from crystal to crystal, certainly indicates an extrinsic origin for at least a sizable part of the absorption for $\alpha \leq 1000\ \mathrm{cm}^{-1}$.[12]

While it cannot be claimed as absolute, evidence from the luminescence spectra of the needles used in the reflectivity experiments suggests that the direct gap is also the fundamental energy gap (Fig. 3). Apart from the main luminescence peak, which varies between 3.44 and 3.47 eV at 4.2 °K, we focus attention on the high-energy tail which shows evidence of luminescence at energies as high as 3.55 eV. Moreover, the shift of the luminescence peak with temperature (Fig. 3) matches in sign and magnitude those seen in the absorption and reflectivity spectra at the direct-gap energy. Hence, these luminescence results set a lower limit of 3.55 eV for any indirect gap in GaN at 2 °K.

We have not been able to obtain definitive information about the $\Gamma - X$ indirect gap in GaN from a study of the mixed crystal GaN_xP_{1-x}. Nitrogen is a strong perturbation in GaP and produces a localized exciton state close to the $\Gamma - X$ indirect gap.[13] The energy of these states does not vary within an experimental error of ± 0.2 meV between $x = 0.000\,01$ and the solubility limit $x = 0.001$. Neglecting bowing, we expect an upward shift of 1.2 meV, since we have shown that the $\Gamma - X$ gap in GaN is at least 1.2 eV larger than in GaP.[12] However, bowing effects are expected to be large for a mixed crystal with a miscibility gap.[14] The general effect of bowing is to reduce (dE_g/dx) for small x and E_g, i. e., near-pure GaP in GaN_xP_{1-x}. Thus the negligible value of $(dE_g/dx)_{x\sim 0}$ observed experimentally might be consistent with a mixed crystal description. However, the validity of such a description can be questioned, since the optical absorption shows that the state due to N in GaP can still be distinguished from the conduction-band tail for $x = 0.001$, even though luminescence studies reveal strong tunneling between adjacent N sites.[13]

In summary, the results of absorption, reflection, and emission experiments on single-crystal GaN at low temperature have established beyond doubt the nature of the absorption edge at ~3.7 eV. Details of this direct gap bear a strong resemblance to those found in ZnO, an analogy which, *a posteriori*, seems very reasonable. No evidence has been found for an indirect fundamental gap, and we conclude that the lowest indirect gap in GaN must exceed 3.55 eV at 2 °K. We also establish an upper limit to $(dE_g/dx)_{x\sim 0}$ for the indirect gap in GaN_xP_{1-x} which is much smaller than indicated by a linear extrapolation between GaP and GaN.

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[7]In some samples both peaks appear in both polarizations. We believe that such mixing is an indication of poorer crystal quality and that the strongly polarized structure in Fig. 2 is more representative of the true reflectance spectrum.

[8]If this direct gap is at $k = 0$, reasonable values of $m_e^* = 0.2$, $m_h^* = 1.0$, and $\epsilon_0 \simeq 10$ give an hydrogenic binding energy of 23 meV for the free exciton, in which case $E_g \sim 3.65$ eV.

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