Photoluminescence from wurtzite GaN under hydrostatic pressure

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The photoluminescence spectrum of undoped epitaxial wurtzite GaN layers on sapphire was measured for applied hydrostatic pressures up to 73 kbar at 9 K and up to 62 kbar at 300 K. The pressure dependences of the I_2 exciton recombination line and the ''yellow'' band (2.2 eV band at ambient pressure) were examined at 9 and 300 K, and the series of donor-acceptor-pair emission lines was analyzed at 9 K. From the I_2 lines, it was found that the band gap increases with pressure by 4.4 ± 0.1 meV/kbar at 9 K and 4.7 ± 0.1 meV/kbar at 300 K. © *1995 American Institute of Physics.*

The III–V nitride semiconductors are attractive candidates for fabricating high speed electronic devices[1,2] and optical devices that are active from the red into the UV.[1] In particular, GaN is of interest for its potential as a blue and UV light emitter. This has spurred intensive experimental and theoretical research to understand the electronic structure of wurtzite and zinc-blende GaN, including the values of the band gaps and the location of critical points.[2–5] In particular, the pressure dependence of the photoluminescence (PL) of GaN is very useful in understanding the electronic energy band structure and structural properties. The pressure dependence of the band gap for wurtzite GaN at room temperature has been measured previously up to 55 kbar by transmission spectroscopy[3] and the band gap of zinc-blende GaN has been measured at 10 K up to 50 kbar by PL.[4] In this investigation, the pressure dependence of the band gap for wurtzite GaN is determined at 9 K up to 73 kbar and at 300 K to 55 kbar by using the I_2 line of the PL spectrum. In the course of this work the effect of applied pressure on other radiative features at 9 and 300 K is also examined.

The unintentionally doped wurtzite GaN epilayer under study was grown by low-pressure organometallic vapor phase epitaxy on a (0001) sapphire substrate surface and was 3.2 μm thick.[2] This thick single-crystalline epitaxial layer is incommensurate because of the large lattice mismatch ($\sim$14%) between the GaN film and the substrate, though there may be a slight strain in the film due to differential thermal contraction of the film and substrate after cooling from the growth temperature.[1,2] Measurements were conducted on thinned samples in a diamond anvil cell that was loaded with liquid argon to attain quasihydrostatic conditions. PL was excited by the 325 nm line (3.81 eV) from a He–Cd laser directed onto the GaN film (0.16 mW), and was collected in ''backscattering'' configuration. It was dispersed by a 0.85 m double spectrometer, and then detected by a cooled photomultiplier. After the pressure was released, the PL spectrum was found to be the same as it was before pressure was applied.

Representative PL spectra at 9 and 300 K are presented in Fig. 1. At 9 K, the biggest peak is the I_2 line (3.472 eV at 1 bar), which corresponds to the recombination of an exciton bound to a neutral donor. A series of donor-acceptor-pair (DAP) emission lines (zero phonon line at 3.271 eV for 1 bar) and the ''yellow'' band (2.2 eV band at ambient pressure) are also strong in the PL spectrum at 9 K. The peak of the I_2 line is over an order of magnitude larger than that of the ''yellow'' band. At room temperature, the ''yellow'' band is the dominant emission, the I_2 line is weak but still measurable, and the DAP lines are absent (Fig. 1). The relative PL intensity of these features is known to be very sensitive to laser intensity[6] and temperature. The dependence of the detection sensitivity of the optical apparatus on wavelength was determined by using tungsten and xenon lamps; the spectra in Fig. 1 have been corrected for variations in spectral sensitivity. This calibration procedure proved to be very

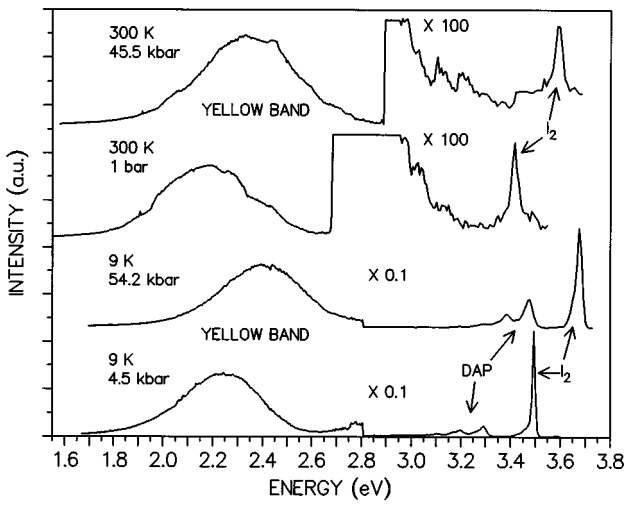

FIG. 1. PL spectra of undoped GaN epitaxial layers at selected pressures at 9 and 300 K. These spectra have been calibrated for variations in detection sensitivity with wavelength, and the vertical scale is the same for the four spectra.

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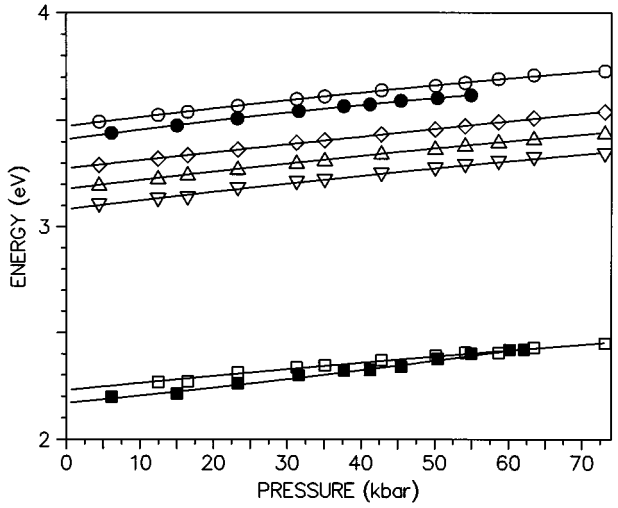

FIG. 2. The dependence of the PL peak energies of the I_2 line (○ at 9 K, ● at 300 K), the "yellow" band (□ at 9 K, ■ at 300 K), and the DAP lines (zero phonon (◆), one phonon (△), and two phonon (▽) lines at 9 K) as a function of pressure. The data points are plotted, along with curve fits using the parameters listed in Table I.

important in determining the relative heights of the DAP phonon replicas and the line shape and peak position of the "yellow" band as pressure was changed.

Figure 2 plots the peak energies of these spectral features as a function of hydrostatic pressure at both temperatures. The pressure dependence of the peak energy (E) of each feature is characterized by fitting the data to:

$$E(P)=E_0(P=1 \text{ bar})+\alpha P+\beta P^2, \tag{1}$$

where P is the pressure in kbar. The fitting constants are listed in Table I, and the fits are displayed along with the data points in Fig. 2. Measurements of the I_2 line at 9 K were conducted only up to 73 kbar, because at this pressure the band gap approached the energy of the laser photons. Though at 300 K it is possible to conduct such measurements at even higher pressures, the position of the I_2 line could not be determined at pressures higher than 55 kbar because of the poor signal-to-noise ratio, due to fluorescence from the diamond anvils and interference from the 340 nm plasma line from the He–Cd laser. At 300 K, the "yellow" band was analyzed up to 62 kbar.

The pressure dependence of the I_2 line is sublinear at both 9 and 300 K, though more so at 300 K. α and β for this line at 300 K are almost the same as those for the band gap E_g obtained from the absorption edge (see Table I).[3] Also, at 9 K these parameters are nearly the same as those seen for zinc-blende GaN (see Table I). The line shape of the I_2 line remains the same up to 73 kbar; its intensity is fairly constant up to ~55 kbar and then it decreases with increasing pressure. The I_2 line is not split at ambient pressure so biaxial strain, from lattice mismatch or differential thermal contraction during cooldown after growth, is small. A splitting, or a change in splitting, would be expected for commensurate layers as pressure is applied, when the epilayer and substrate have very different elastic constants,[7] as is true for GaN and sapphire.

TABLE I. Energy positions and pressure coefficients for the PL peaks, using the fit of Eq. 1.

	$E(0)$ (eV)	α (meV/kbar)	β (10^{-2} meV/kbar^2)
I_2 line			
9 K	3.472±0.002	4.4±0.1	−1.1±0.2
300 K	3.411±0.002	4.7±0.1	−1.6±0.2
DAP lines (9 K)			
Zero LO	3.271±0.001	4.0±0.1	−0.5±0.1
One LO	3.178±0.001	4.2±0.1	−0.8±0.1
Two LO	3.082±0.004	4.3±0.3	−0.8±0.4
Yellow band			
9 K	2.23±0.01	3.4±0.3	−0.5±0.4
300 K	2.17±0.01	3.3±0.8	1.3±0.6
From other published work			
Eg (300 K)[a]	3.41–3.46[d]	4.7	−1.8
DAP (ZB) (10 K)[b]	3.199	4.5	−2.8
FB (ZB) (10 K)[c]	3.268	4.4	−1.7

[a]The wurtzite GaN band gap obtained from the absorption edge in Ref. 3.
[b]The donor-acceptor line of zinc-blende (ZB) GaN in Ref. 4. It is assumed that the quadratic parameter listed in this reference is β and not d^2E/dP^2 as claimed because $d^2E/dP^2=2\beta$.
[c]The free-electron to bound-hole line of zinc-blende GaN in Ref. 4. See the comment in b.
[d]The value of the band gap measured at ambient pressure may vary from sample to sample due to their different electron concentrations (Ref. 3).

The parameters that characterize the pressure dependence of the zero phonon DAP line and the first and second LO phonon replicas of this line are presented in Table I. The magnitudes of the linear and quadratic pressure coefficients of the DAP lines for wurtzite GaN are smaller than those for the I_2 line, and are also smaller than those for the DAP lines in zinc-blende GaN (see Table I). As pressure is increased, the relative intensities of the zero, first and second phonon replicas of the DAP lines in wurtzite GaN (9 K) do not change, remaining in the ratio 1:0.5:0.2. This is seen in Fig. 1, which has been corrected for spectral response variations.

The intensity of the "yellow" band changes by less than 10% as the pressure is increased up to 73 kbar (Fig. 1). From Table I, the linear coefficient α is seen to be significantly smaller than those of the I_2 and DAP lines.

The pressure dependence of the I_2 line at 300 K is the same as that of the band gap determined by the absorption edge, which would suggest that the binding energy of an exciton bound to a neutral donor does not change appreciably with pressure. Though the application of pressure increases the binding energy of a shallow exciton because of an increase in the electron effective mass and a decrease in the dielectric constant, the pressure-induced change of its binding energy is expected to be quite negligible (<1%), as is seen by using the effective-mass approximation.[4,8] Therefore, it is reasonable that the pressure dependence of the I_2 line at 9 K should be the same as that of the band gap at 9 K.[7]

The magnitude of β for the I_2 line in wurtzite GaN at 9 K determined here is smaller than that for the free electron-bound hole (FB) transition line in zinc-blende GaN (Ref. 4) (Table I), while the values of α for both structures are the

same within experimental uncertainty. Any such differences could be attributed to the different pressure dependences of the band gaps in wurtzite and zinc-blende GaN, since the I_2 and FB lines should track the band gaps in these respective materials. These trends are consistent with the tendency of the results of the theoretical work of Ref. 5, which gives α=3.9 meV/kbar and $\beta=-3.2\times10^{-2}$ meV/kbar^2 for the band gap in wurtzite GaN, and α=4.0 meV/kbar and $\beta=-3.8\times10^{-2}$ meV/kbar^2 for the band gap in zinc-blende GaN.

Using the configuration coordinate model,[9] the constant relative intensities of the DAP phonon replicas with changing pressure (9 K) suggest that the relative equilibrium positions of the donor and acceptor state energy curves and the curvatures of these curves change very little as pressure increases. α for the DAP lines depends on the increase in the energy separation of the donor and acceptor states, which tracks the band gap change, and the pressure-induced changes in phonon energies. The difference in α for adjacent DAP lines is ~0.1–0.2 meV/kbar. If this difference were due to the changing LO phonon energy in the acceptor state with pressure, then this pressure dependence would be larger than that previously measured for TO phonons in wurtzite GaN, 0.05 meV/kbar.[10]

Early work[11] suggested that the ''yellow'' band is due to a shallow donor-deep acceptor transition. However, more recently Ref. 12 has concluded that this band is associated with radiative recombination between the neutrally charged deep donor state and effective-mass (EM) acceptor states. Within the configuration coordinate model, the equilibrium displacements of the deep donor and the acceptor energy curves may be very different. This could explain why the ''yellow'' band energy is much lower than the band gap energy (due to ''strong phonon coupling'') and why this band is very broad (due to overlapping phonon replicas).[11] The width of this band is essentially independent of pressure; the full width at half height is 0.38 eV at 9 K for all pressures studied and it increases only from 0.44 eV (1 bar) to 0.46 eV (45 kbar) at 300 K, and this change is within experimental uncertainty. Consequently, the degree of phonon coupling, characterized by the Huang–Rhys factor, does not appear to change with pressure.

The pressure dependence of the energy of deep-center-related lines in several semiconductors has been explained by considering the movement of these centers relative to the band valleys in the semiconductor. For example, in zinc-blende GaN, α for two deep centers (2.7 and 1.8 meV/kbar) are much smaller than those of the FB and DAP (4.4 and 4.5 meV/kbar).[4] These smaller pressure coefficients have been related to the average of the coefficients for different conduction band valleys,[4,13] which suggests that these centers are very delocalized. The calculations in Ref. 5 suggest that in wurtzite GaN α is largest for the $\Gamma_v-\Gamma_c$ gap (3.9 meV/kbar), a little smaller for Γ_v-A_c (3.6 meV/kbar), and is much smaller for all other Γ_v-conduction band critical point gaps. A deep donor state that is localized at or in between Γ_c and A_c would have an α about equal to that of the band gap. A deep donor state extended over a wider region in the Brillouin zone would have an α smaller than that of the energy gap, as is observed here. α weighted over the entire Brillouin zone is ~1.7 meV/kbar, using the results from Ref. 5, which is significantly smaller than that measured here and suggests that the deep center is somewhat localized near Γ_c and/or A_c.

In summary, the pressure dependences of the band gap in wurtzite GaN at 9 and 300 K have been determined from the shift of the peak position of the I_2 line with pressure; the dependence at 300 K is similar to that determined from band-edge absorption. The changes of the DAP lines and the ''yellow'' band upon compression have been described in the terms of the band and configuration coordinate models.

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