Photoluminescence and reflectance studies of exciton transitions in wurtzite GaN under pressure

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We have measured photoluminescence (PL) and reflectance spectra of high-quality wurtzite GaN on sapphire at pressures up to 8 GPa ($T=10$ K). All three intrinsic exciton transitions arising from the A, B, and C interband transitions were observed in reflectance measurements. The PL spectra are dominated by the A and B free exciton transitions and the recombination of an exciton bound to a neutral donor. Transitions due to the excited $n=2$ state of the A exciton and the first- and second-order LO phonon replicas of the A free exciton were also resolved. The pressure dependence of the A band gap and exciton binding energy is obtained from the intrinsic exciton energies. The experimental results clearly reveal a sample-dependent change of the biaxial strain in the GaN layers with increasing hydrostatic pressure. [S0163-1829(98)02635-6]

The recent breakthrough and success in the fabrication of GaN-based blue-light emitting devices[1] has generated much interest in the investigation of the intrinsic properties of wurtzite GaN. Most optical studies have been concerned with the donor-acceptor bound exciton recombination, the shallow donor-acceptor pair emission, and the origin of the deep yellow band emission.[2–4] Recently, progress has been made on the epitaxial growth of GaN on different substrates with GaN or AlN as a buffer layer. The availability of high optical quality GaN films makes possible the study of *intrinsic* free exciton transitions by photoluminescence (PL) and reflectance measurements.[5]

The pressure dependence of PL emission yields valuable information on the electronic band structure and optical properties. Several groups have performed high-pressure measurements on wurtzite GaN.[6–9] The main emphasis of these studies was on the extrinsic optical transitions. Here, we present PL and reflectance measurements of high-quality wurtzite GaN under high pressure up to 8 GPa. The pressure dependences of the free and bound excitons, the LO phonon replicas of the A exciton, as well as the excited A exciton energies are determined.

Two nominally undoped GaN epilayers studied in this work were grown on (0001) sapphire substrates. Sample 1 was grown by molecular-beam epitaxy with a 200-nm AlN buffer layer. The thickness of the GaN layer is 6 μm. Sample 2 was grown by low-pressure metal-organic chemical-vapor deposition. The deposition sequence consists of a thin (50–100 nm) AlN buffer layer followed by a 3.8-μm GaN epilayer. High-pressure reflectance and PL measurements were performed at 10 K by using a diamond-anvil cell (DAC) in combination with a helium-flow cryostat. To fit into the DAC gasket hole, the samples were mechanically thinned to a total thickness of about 30 μm (sample 1) and 50 μm (sample 2) and then cleaved into pieces of about 100 $\times 100$ μm^2. Condensed helium was used as a pressure transmitting medium. The PL was excited by the 325-nm line of a He-Cd laser and collected in backscattering configuration. Both reflected light and PL emission were dispersed by a 0.6-m single-grating spectrometer and detected by a GaAs photomultiplier operating in fast photon-counting mode. For the reflectance measurements, the light from a xenon arc lamp was focused on a pinhole 100 μm in diameter, which was imaged with about unity magnification onto the sample surface.

Figure 1 shows representative reflectance and PL spectra for sample 1 measured at 10 K and at ambient pressure.

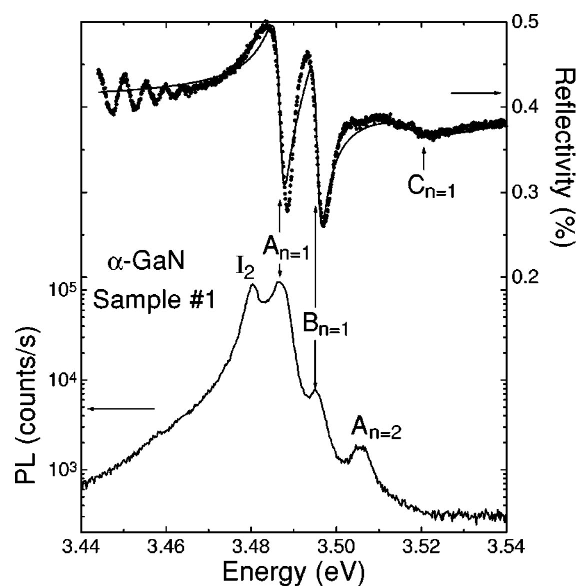

FIG. 1. Photoluminescence and reflectance spectra of wurtzite GaN (sample 1) at 10 K and ambient pressure.

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Three well-resolved structures, labeled as $A_{n=1}$, $B_{n=1}$, and $C_{n=1}$, can be observed in the reflectance spectrum. The solid line passing through the experimental points represents the result of a least-squares fit based on a four-branches polariton dispersion taking into account spatial dispersion and Pekar boundary conditions.[10] Using the notation of Ref. 10, we obtain the following fitted parameters: $E_A=3.4865$, $E_B=3.4953$, and $E_C=3.5185$ eV for the exciton energies, $4\pi\alpha_A=2.042\times10^{-3}$, $4\pi\alpha_B=1.667\times10^{-3}$, and $4\pi\alpha_C=2.079\times10^{-3}$ for the polarizabilities, and $\Gamma_A=2.44$, $\Gamma_B=2.14$, and $\Gamma_C=22.3$ meV for the linewidths. Here we assume the effective mass of the excitons to be equal to the electron mass. We observe four PL peaks in the same energy range of the reflectance spectrum. The peak energies in the PL are $E_A=3.4867$ and $E_B=3.4951$ eV, which are very consistent with the fit results of the reflectance spectrum and show no Stokes shift.

For wurtzite GaN, the bottom of the conduction band is mainly constructed from the s states of Ga while the upper valence band is essentially obtained from the three p states of N.[11] At the center of the Brillouin zone, GaN transforms under the point group C_{6v}. For backscattering configuration where $\vec{E}\perp c$, the A exciton ($\Gamma_7\leftrightarrow\Gamma_9$), and the B and C excitons ($\Gamma_7\leftrightarrow\Gamma_7$) are optically active transitions according to the selection rules.[12] Therefore, we assign the features $A_{n=1}$, $B_{n=1}$, and $C_{n=1}$ to be the intrinsic exciton transitions associated with the A, B, and C bands and $A_{n=2}$ as the first excited state of the A exciton. We also assign the emission at 3.48 eV to be the bound exciton I_2 peak. This assignment is confirmed by our study of the PL at different temperatures and excitation densities. The intensity of the I_2 peak quickly decreases with increasing temperature or laser power density relative to that of the other exciton transitions. Thus, I_2 can be attributed to the transition of an exciton bound to a neutral donor.[8]

Figure 2 shows reflectance and PL spectra for sample 1 at 10 K and different pressures. After the substrate was thinned for pressure measurements, all optical transition energies of sample 1 decreased by about 7 meV. This effect was absent in sample 2. Sample 1 had the thicker GaN layer and thinner sapphire substrate compared to sample 2. Thus, the redshift of transition energies is attributed to a partial relaxation of the residual biaxial strain in the GaN layer, which, according to empirical data of Refs. 13 and 14, decreases from 0.066% to 0.025%. The strain relaxation in sample 1 may involve a bending due to thinning below some critical thickness. The PL and reflectance line shapes are independent of pressure, which enables us to determine the pressure dependence of the exciton energies quite accurately. In addition to the free and bound exciton transitions, two additional PL peaks, labeled as LO and 2LO in Fig. 2(b), are observed. Energy differences between these two peaks and the A exciton are close to integer multiples of the LO phonon energy. Thus, we assign the LO and 2LO peaks to be the first- and second-order phonon replicas of the A exciton. The pressure dependence of the energy difference [inset of Fig. 2(b)] observed here is in agreement with the LO phonon shift obtained by high pressure Raman scattering[15] (solid lines). In Fig. 2 we observe a continuous blueshift for all exciton transitions in both reflectance and PL with increasing pressure. The intensities essentially remain constant with pressure, ruling out a degradation of the sample quality with increasing pressure.

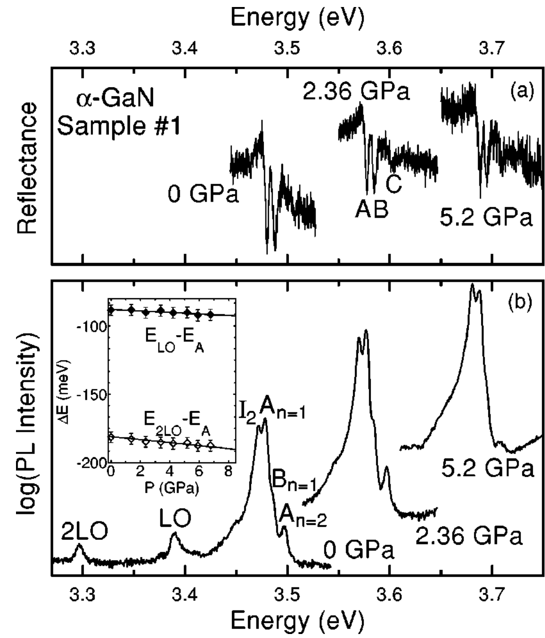

FIG. 2. PL and reflectance spectra of GaN (sample 1) at 10 K and several pressures. The inset shows the pressure dependence of the energy difference between the LO phonon replicas and the A exciton.

The ground and excited A exciton energies vs pressure for sample 1 are plotted in Fig. 3. The solid lines represent the results of least-squares fits to the experimental data using quadratic relations. The fitted results for the A exciton as well as the B,C,I_2, and excited A excitons are listed in Table I. For all observed exciton transitions, the quadratic coeffi-

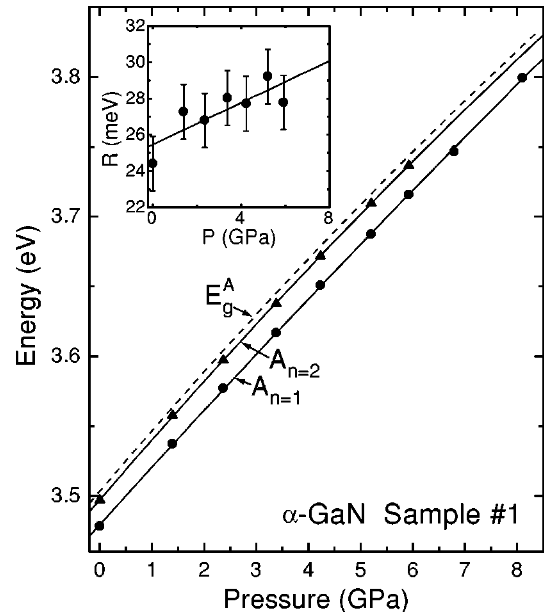

FIG. 3. Free exciton energies of GaN (sample 1) as a function of pressure. The dashed line represents the pressure dependence of the A band gap. The inset shows the A free-exciton binding energy as a function of pressure. Solid lines represent results of least-squares fits.

TABLE I. Energies and pressure coefficients of exciton transitions in wurtzite GaN layers as obtained from fitting a quadratic relation $E(P)=E(0)+a_1P+a_2P^2$ to the experimental data. The numbers in parentheses give the experimental error in units of the last decimal place. Results of the A band gap and its binding energy are also listed.

Sample	Peak	$E(0)$ (eV)	a_1 (meV/GPa)	a_2 (meV/GPa^2)
1	I_2	3.473(3)	41.5(15)	−0.3(2)
	$A_{n=1}$	3.479(2)	41.4(10)	−0.3(1)
	$B_{n=1}$	3.487(3)	41.0(16)	−0.2(2)
	$C_{n=1}$	3.507(5)	40.5(28)	−0.2(3)
	$A_{n=2}$	3.497(2)	43.4(11)	−0.5(2)
	$E_g(A)$	3.503(2)	43.8(14)	−0.5(2)
2	I_2	3.482(2)	38.3(9)	−0.3(1)
	$A_{n=1}$	3.489(2)	38.6(9)	−0.3(1)
	$B_{n=1}$	3.499(2)	37.8(15)	−0.2(2)

cients are very small. For sample 2, we measured only the 10-K PL spectra under pressure up to 8 GPa. Optical transitions related to A and B excitons and the neutral donor bound exciton were resolved. The pressure dependence of these exciton energies shows a blueshift similar to that of sample 1. The results for sample 2 are also listed in Table I.

The observation of the $A_{n=1}$ and $A_{n=2}$ transitions enables us to determine the A exciton binding energy. In the framework of the effective-mass approximation and under the assumption of a hydrogenlike model the energy levels E_n of the exciton states and the exciton binding energy R can be written as

$$E_n=E_g-\frac{R}{n^2}, \tag{1}$$

$$R=\frac{R_H}{m_0\epsilon_0{}^2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right)^{-1}, \tag{2}$$

where E_g is the direct band gap, n is the principal quantum number, $R_H=13.61$ eV is the $1s$ binding energy of hydrogen, m_0 is the free electron mass, m_e and m_h are the effective electron and hole masses, and ϵ_0 is the low-frequency dielectric constant. In the case of wurtzite GaN these equations should be modified because the reduced effective masses as well as the dielectric constant are anisotropic. However, it has been demonstrated that, to a good approximation, the isotropic reduced spherical masses and dielectric constant still can be used to estimate the exciton binding energy.[16]

Using Eq. (1) and the experimental $A_{n=1}$ and $A_{n=2}$ energies, we obtain the A free-exciton binding energies as represented by the data points in the inset of Fig. 3. The fitted solid line corresponds to $R_{P=0}=25.5(15)$ meV and $dR/dP=0.6(4)$ meV/GPa. For comparison, from Eq. (2) we calculate $R_{P=0}=24$ meV using $m_e=0.2m_0$, $m_h=0.8m_0$, and $\epsilon_0=9.5$.[17] GaN has a large band gap and small spin-orbit splitting;[18] therefore the changes of the effective masses under pressure can be determined by the three-band $\mathbf{k}\cdot\mathbf{p}$ model.[19] The corresponding effect on the binding energy is $dR/dP=0.2$ meV/GPa. In addition, the dielectric constant is expected to decrease under pressure.[6] Thus, although the experimental pressure coefficient of R has a large error bar, its value appears to be consistent with model predictions.

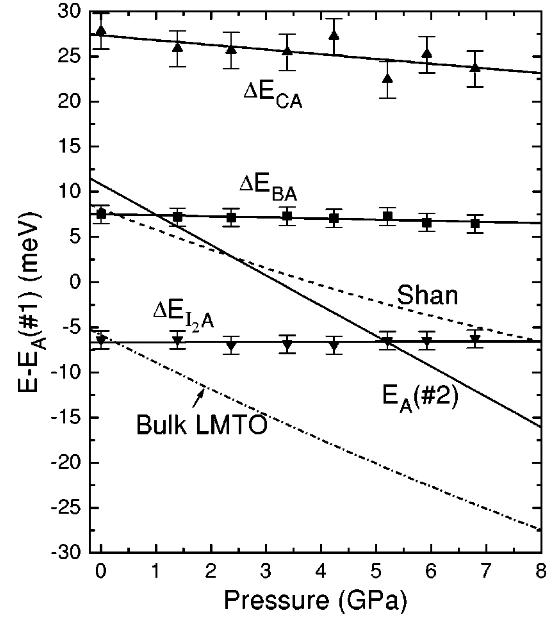

FIG. 4. Pressure dependence of the energy splitting between the free (bound) excitons of sample 1 (closed symbols). The A free-exciton energy is taken as reference energy. The curve labeled E_A (#2) refers to the A free-exciton energy of sample 2 relative to that of sample 1. The dotted and dash-dotted lines indicate experimental and theoretical results, respectively, taken from the literature (see text).

The exciton energies of GaN epilayers depend on the residual biaxial strain. Under biaxial compression both A and B exciton energies increase linearly with identical slope while the C exciton energy shows a larger blueshift.[13,14] Therefore, it can be expected that a change of the lattice mismatch between the GaN and buffer layers induced by the external hydrostatic pressure affects the exciton energies. As the samples we studied are grown on the sapphire/AlN buffer layers, the GaN epilayer is initially subjected to a compressive biaxial strain. The hydrostatic compression behavior of bulk AlN and GaN has been studied,[20] but the results of the ambient pressure bulk moduli (B_0) are somewhat scattered. Considering a systematic trend within the group-III nitrides and the fact that the zero pressure molar volume of AlN is about 8% smaller compared to that of GaN, we can expect that the B_0 of AlN is larger than that of GaN (about 200 GPa), but smaller than that of sapphire ($B_0=254$ GPa, Ref. 21). Thus, an external hydrostatic pressure is expected to induce a net decrease of the nonisotropic strain component in the GaN epilayer.

In order to show more clearly the small but perceivable effects of nonisotropic strain on the hydrostatic pressure dependencies, we plot the energy differences between the free and bound excitons and the $A_{n=1}$ exciton of sample 1 against pressure in Fig. 4. Solid symbols represent the experimental data, and solid lines correspond to results of least-squares fits. Also shown is the energy difference of the $A_{n=1}$ exciton energy in sample 2 relative to that of sample 1.

According to Fig. 4, several specific behaviors can be

observed. The energy differences E_{I_2A} is essentially independent on pressure. Also the splitting E_{BA} for sample 1 changes very little with pressure, which is in agreement with the strain independence of the B and A exciton splitting under compressive strain.[13,14] The very weak pressure dependence of E_{CA} would suggest that there is no significant change of the biaxial strain in sample 1 with increasing hydrostatic pressure. However, in such reasoning we would have to assume that we can neglect pressure-dependent bending of the sample and a change of the internal positional parameter u, which at ambient pressure is very close to the ideal value of 3/8. The difference between the $A_{n=1}$ free-exciton energies in samples 2 and 1 is 12 meV at ambient and decreases noticeably with pressure, even reverses sign. An epilayer with similar thickness of the AlN buffer layer and GaN layer to that of sample 2 has been studied by Shan *et al.*[7] (dashed line in Fig. 4). Their results are intermediate between those for samples 1 and 2, as shown by the dashed line in Fig. 4. At zero pressure the compressive strain in sample 2 is obviously larger than that in sample 1. The change of the $A_{n=1}$ exciton energy of sample 2 with respect to that of sample 1 indicates a different evolution under pressure of the biaxial strain. We consider a pressure dependence of bending effects in sample 1 as a possible reason.

For comparison, a theoretical result[22] is shown by the dash-dotted line in the same figure. A rigid energy shift to the theoretical results has been applied to account for the so-called gap error inherent in calculations based on the local-density approximation.[23] The energy differences shown in Fig. 4 are very small compared to the overall shift of the band-gap energy with pressure. Thus, the theoretical calculation can be considered to be in very good agreement with the various experimental data.

In summary, we have studied PL and reflectance spectra of high-quality wurtzite GaN layers on sapphire as a function of pressure at 10 K. The pressure dependence of the A band gap and exciton binding energy is obtained from the ground and first excited A exciton energies. Within the effective-mass approximation, the increase of the A exciton binding energy can be accounted for in terms of the increasing electron effective mass and decreasing dielectric constant with pressure. The exciton energies as a function of pressure clearly reveal that the application of hydrostatic pressure results in a change of the biaxial strain in the GaN layers, which differs for samples characterized by different thicknesses of GaN layer, AlN buffer layer, and sapphire substrate. In order to determine the true hydrostatic pressure dependence of exciton energies in GaN, it would be very useful to study epitaxial layers of GaN grown on bulk GaN substrates.

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