Spin-exchange splitting of excitons in GaN

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(Received 30 March 2001; published 23 August 2001)

We report on polarization-dependent photoluminescence measurements in thick GaN layers. The free-exciton emission peaks are found to appear at different energy positions in the spectra polarized perpendicular and parallel to the *c* axis. In the case of $\mathbf{E}\|c$ polarization, emission from the spin-triplet state of the *A* exciton is observed and the singlet-triplet splitting resulting from the exchange interaction is obtained. In a highly strained layer, the splitting between the two dipole-allowed states of the *B* exciton is also observed. The experimental data are analyzed using an appropriate exciton Hamiltonian in a wurtzite crystal. The stress dependence of the energy splitting between the exciton states is studied and the exchange interaction constant in GaN, $\gamma = 0.58 \pm 0.05$ meV, is determined.

DOI: 10.1103/PhysRevB.64.115201 PACS number(s): 71.35.−y, 71.45.Gm

I. INTRODUCTION

The development of group-III nitride optoelectronic devices operating in the visible and near-ultraviolet spectral region demands better understanding of the fundamental electronic and optical properties of GaN and its related compounds. It is well known that the near bandgap optical properties of GaN are dominated by excitons.[1] In a wurtzite structure, the valence band is split by the combined action of the crystal field and spin-orbit interaction. As a consequence, there are three free-exciton series commonly denoted *A*, *B*, and *C*. The binding energy of the *A* exciton in GaN is 25–26 meV (Refs. 2–4) implying a dominance of the excitonic recombination processes up to the room temperature. Almost the same value has been suggested for the binding energies of the *B* and *C* excitons.[3] Since the GaN layers are usually grown on foreign substrates (sapphire, SiC, ZnO, Si), they always experience a large built-in strain due to the difference in the lattice constant and thermal expansion coefficient between the GaN and the substrate. This strain is found to influence strongly the exact energy positions and oscillator strengths of the excitons.[5] Despite a considerable amount of detailed studies, the exciton fine structure resulting from the electron-hole exchange interaction is still a subject of fundamental research and discussion. The exchange interaction is known to lead to a splitting of the spin-singlet states from the spin-triplet states and also to the longitudinal-transverse splitting of the spin-singlet states.[6] The splitting is expected to be of the order of 1–2 meV in GaN (Refs. 1,5) but the large exciton linewidth in the samples so far available prevents the substructure to be resolved.

The longitudinal-transverse splitting Δ_{LT} is usually extracted from the reflectance line shape fitting. Such a procedure is not straightforward in GaN because the crystal field and spin-orbit splitting parameters are rather small and the different excitons cannot be treated separately as in the case of II-VI compounds. Instead, the simultaneous coupling of the electromagnetic wave with the *A*, *B*, and *C* excitons must be taken into account.[7] Moreover, the fitting is very sensitive to the thickness of the dead layer and to the exciton effective masses which are not exactly known. As a result, different values for the longitudinal-transverse splitting in GaN have been reported. For example, Shan *et al.*[8] determined $\Delta_{LT} = 1$ meV for the *A* exciton in a 2.5-μm-thick GaN layer grown by metalorganic vapor phase epitaxy (MOVPE) on *c*-plane sapphire, while the value obtained by Gil *et al.*[9] in a similar sample is $\Delta_{LT} = 2.9$ meV. We should emphasize that the longitudinal-transverse splitting is roughly proportional to the exciton oscillator strength and depends on the strain, especially in the case of *B* and *C* excitons.[10] In a homoepitaxial GaN, the longitudinal-transverse splitting of *A*, *B*, and *C* excitons has been found to be 0.9, 1.04, and 0.37 meV, respectively.[7] Rather similar values (1.34, 1.17, and 0.273 meV) have been obtained in a free-standing GaN grown by the lateral epitaxial overgrowth (LEO) technique.[11]

The determination of the singlet-triplet splitting is even more difficult because a photon propagation perpendicular to the *c* axis is required. Nevertheless, Eckey *et al.*[12] succeeded in determining the singlet-triplet splitting of the *A* exciton in a 400-μm-thick heteroepitaxial GaN. By a deconvolution of the entire excitonic emission spectra they obtained a value of 0.120 ± 0.1 meV. In a homoepitaxial GaN layer, the singlet-triplet splitting of 0.91 ± 0.05 meV has been derived from magnetoreflectance data.[13] Recently, Reynolds *et al.*[14] reported a singlet-triplet splitting of 2.9 meV, which can be reasonable for more ionic II-VI compounds but seems to be rather large for the GaN.

In this paper, we present the results from polarized photoluminescence (PL) measurements in thick GaN layers grown by hydride vapor phase epitaxy (HVPE). The PL spectra for both $\mathbf{E}\perp c$ and $\mathbf{E}\|c$ polarization exhibit well resolved free-exciton peaks and reveal the internal structure of the excitons. The observed exciton transitions are interpreted within the framework of general group theory. The experimentally obtained splitting between the exciton states is compared with those resulting from the diagonalization of the exciton Hamiltonian in a strained wurtzite crystal.

II. EXPERIMENT

The two GaN samples used in this study were grown in a horizontal HVPE system at atmospheric pressure and at a growth temperature of 1080 °C.[15] The first sample was grown directly on *c*-plane oriented sapphire, and has a thick-

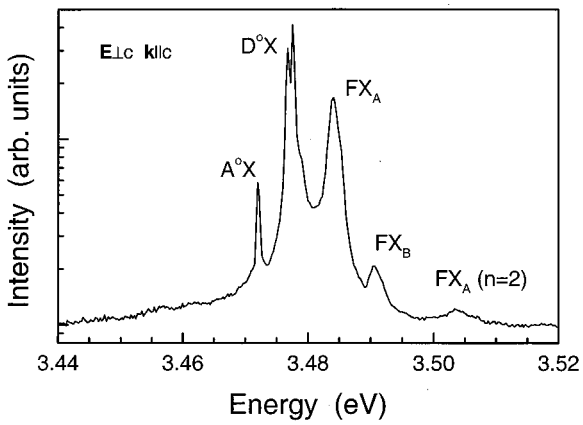

FIG. 1. Unpolarized photoluminescence spectrum of a 80-μm-thick GaN layer for the $\mathbf{k}\|c$ configuration.

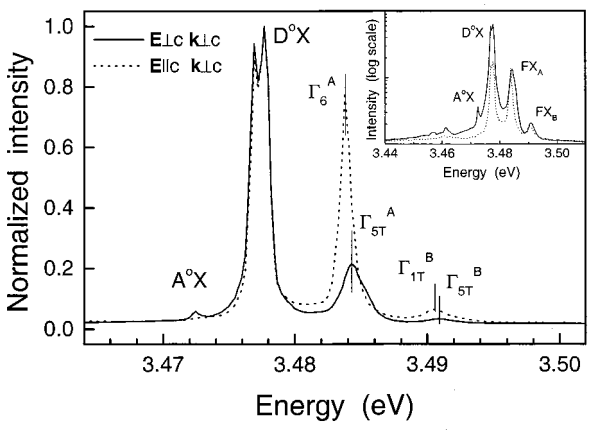

FIG. 2. Normalized photoluminescence spectra of a 80-μm-thick GaN layer for σ polarization (solid line) and π polarization (dotted line). The inset shows the spectra in a logarithmic scale.

ness of about 80 μm. The second sample was a 130-μm-thick free standing layer. It was also grown on *c*-plane sapphire, but with an undoped MOCVD GaN buffer. Afterwards, the sapphire substrate was removed by a laser lift-off technique.[16] The PL spectra were measured at 4 K, with excitation by the fourth harmonic of a continuous wave Nd:vanadate laser ($\lambda_{exc}=266$ nm). The excitation intensity was kept below 1 W/cm^2. The luminescence signal was dispersed by a Czerny-Turner type monochromator and detected by a cooled charge coupled detector (CCD). A Glan-Thomson prism and a depolarizer were used in front of the monochromator to select the polarization of the detected signal. The calibration of the system was performed with the emission lines of a low-pressure Ne lamp. To evaluate the correct wavelength-to-photon energy conversion, the refractive index of the air $n=1.0002861$ was used. The spectral resolution was 0.2 meV in the region of 350 nm.

III. EXPERIMENTAL RESULTS

Figure 1 shows the PL spectrum of the 80 μm thick layer for α polarization ($\mathbf{k}\|c, \mathbf{E}\perp c$). The strongest PL peak, labeled D^0X, corresponds to the donor-bound exciton emission. It is a doublet with an energy separation of 0.8 meV. The two components exhibit a full-width at half-maximum (FWHM) of 0.7 meV indicating a high quality of the sample. Such a complex structure of the donor-bound exciton emission is commonly observed in homoepitaxial GaN layers, where up to five lines have been detected.[4] We attribute the two D^0X components in our sample to a presence of two separate shallow donors. Below the D^0X emission there is another sharp peak (FWHM$=0.6$ meV), labeled A^0X. This peak has been controversially ascribed as a deeper donor-bound exciton[17] or as an ionized donor-bound exciton,[18] but the recent results suggest that it corresponds to an exciton bound to a neutral acceptor.[4,19] The sample exhibits well pronounced emission peaks (FWHM≈ 2 meV) of *A* and *B* free excitons FX_A and FX_B. The broad feature around 3.503 eV is most probably due to the emission from the excited states of the *A* exciton. The assignment of the exciton PL peaks is confirmed by the reflectance spectrum of the same sample.[19] The energy positions of the peaks are blueshifted by 7 meV in comparison with those in homoepitaxial GaN layers[4] implying that the sample is under biaxial compressive stress ($\tau_{xx}=\tau_{yy}$). Using $E_A^0=3.4771$ eV (Ref. 4) as a reference energy for the *A* exciton in a strain-free GaN and assuming a linear dependence on the in-plane stress, i.e., $E_A=E_A^0+\beta\tau_{xx}$, we estimate $\tau_{xx}=2.9\pm0.3$ kbar. For the calibration coefficient β, an average value between 2.2 meV/kbar (Refs. 3 and 20) and 2.7 meV/kbar (Ref. 21) was used.

Figure 2 presents the PL spectra of the same sample for $\mathbf{E}\perp c$, $\mathbf{k}\perp c$ (σ polarization) and $\mathbf{E}\|c$, $\mathbf{k}\perp c$ (π polarization). In this geometry, the laser beam was focused on the side facet of the sample by a microscopic objective and the spectra are taken from a spot about 10 μm below the top surface. The PL spectrum for σ polarization resembles the one in Fig. 1. A small variation in the peak energies (less than 1 meV) is probably due to the slight variation of the residual strain at different depth from the top surface of the sample. The π-polarized spectrum, however, behaves quite differently. The intensity of the donor-bound exciton is reduced by a factor of 4, while the acceptor-bound exciton is not even detected (see the inset in Fig. 2). Such a behavior can be understood having in mind that these complexes originate from the *A* exciton, which is dipole-forbidden for $\mathbf{E}\|c$ as will be elucidated below. Accordingly, we might except a decrease of D^0X and A^0X emission lines in this polarization because the same selection rules hold for a free exciton and the exciton complexes arising from it. Furthermore, in the case of $\mathbf{E}\|c$ polarization, the free exciton emission peaks appear at energies lower than those for $\mathbf{E}\perp c$. A shift of 0.530 ± 0.03 meV and 0.240 ± 0.08 meV is observed for the *A* and *B* excitons, respectively. There is also a noticeable decrease of the linewidth of the *A* exciton for $\mathbf{E}\|c$ polarization.

The polarized spectra of the free-standing sample for the $\mathbf{k}\perp c$ configuration are shown in Fig. 3. For $\mathbf{E}\perp c$ polarization, the spectrum reveals a donor-bound exciton emission at 3.4714 eV, an acceptor-bound exciton emission at 3.4662 eV and a broad band emission with an unknown origin around 3.45 eV. The strongest peak in this band can be associated with an exciton bound to a deeper acceptor.[19] In the free-exciton region, only the *A* exciton is clearly observed. As can

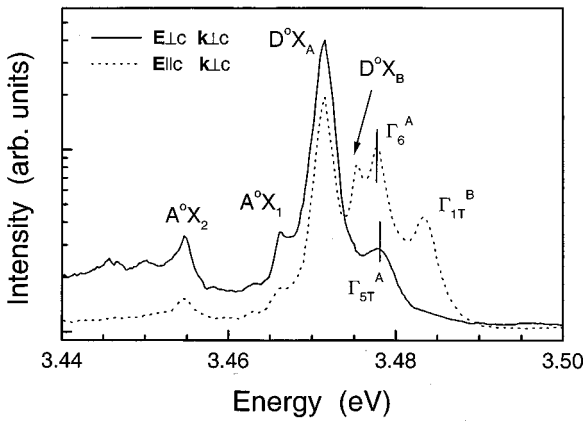

FIG. 3. Polarized spectra of a free-standing GaN sample for $\mathbf{E}\perp c, \mathbf{k}\perp c$ (solid line), and $\mathbf{E}\parallel c, \mathbf{k}\perp c$ (dotted line).

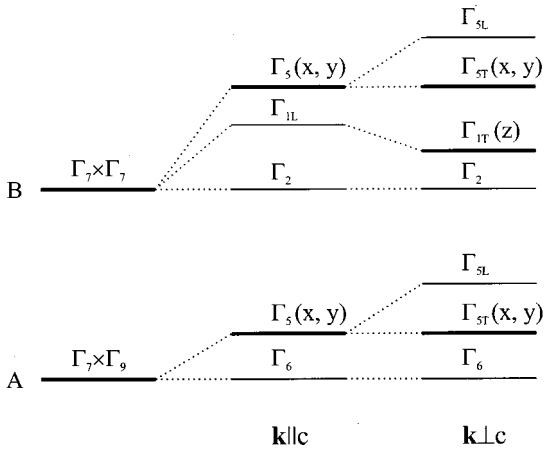

FIG. 4. Schematic diagram of the internal structure of *A* and *B* excitons in a wurtzite GaN. The allowed polarizations are given in parentheses. Thin lines correspond to dipole-forbidden states.

be deduced from the high ratio between the intensities of D^0X_A and FX_A peaks (about 30:1), the density of the residual donors in this sample is higher than in the previous one, where the ratio is only 3:1. This leads to a larger broadening of the free-exciton emission. For $\mathbf{E}\parallel c$ polarization, the linewidth of the *A* exciton decreases and the peak is redshifted by 0.520 ± 0.04 meV. It is interesting that in this configuration, a sharp peak (labeled D^0X_B) is observed between the *A* exciton and the donor-bound exciton D^0X_A. The appearance of this peak obviously correlates with the enhancement of the *B* exciton. Then, we attribute it to a donor-bound exciton involving the hole from the second valence band.[4,22] The peak position of the *A* exciton in $\mathbf{k}\perp c$ configuration (3.478 eV) is very close to that in the homoepitaxial GaN indicating almost complete stress relaxation in this sample. The in-plane stress is estimated to be 0.4 ± 0.1 kbar.

IV. DISCUSSION

The different energy position of the free-exciton peaks in the spectra for $\mathbf{E}\perp c$ and $\mathbf{E}\parallel c$ polarizations suggests that exciton states of different symmetry are detected. The fine structure and symmetry properties of the excitons in GaN can be deduced from the general group theory.[6] Figure 4 illustrates the internal structure of the two lowest excitons of GaN. The *A* exciton comes from the lowest conduction band with Γ_7 symmetry and the topmost valence band having Γ_9 symmetry. The direct product $\Gamma_7\times\Gamma_9$ transforms according to $\Gamma_5+\Gamma_6$ representations. The twofold degenerate spin-triplet state Γ_6 is dipole forbidden, while the twofold degenerate spin-singlet state Γ_5 has an optical dipole momentum perpendicular to the *c* axis and is allowed for $\mathbf{E}\perp c$ polarization. For a wave vector perpendicular to the *c* axis the Γ_5 states form a transverse (Γ_{5T}) and a longitudinal (Γ_{5L}) state, of which the longitudinal one is optically inactive. The Γ_6, Γ_{5T}, and Γ_{5L} exciton states are separated energetically by the spin-exchange interaction. The analytical part of the exchange interaction shifts the Γ_{5T} state above the Γ_6 state, while the Γ_{5L} state is shifted to even higher energy by the long-range nonanalytical part of the exchange interaction. The *B* exciton arises from the lower valence band (with Γ_7 symmetry) and decomposes into four states: Γ_1, Γ_2, and two Γ_5 states. Again the Γ_5 states are optically allowed for $\mathbf{E}\perp c$ polarization and split to a longitudinal and a transverse state at $\mathbf{k}\perp c$. The spin-triplet state Γ_2 is forbidden for both polarizations. The Γ_1 state has an optical dipole momentum oriented parallel to the *c* axis and is allowed only for $\mathbf{E}\parallel c$ polarization. For $\mathbf{k}\parallel c$ the Γ_1 state emerges as a purely longitudinal state. The symmetry properties of the *C* exciton are the same as the *B* excitation, because the third valence band also has Γ_7 symmetry.

According to the above exciton structure, we interpret the two free-exciton peaks for $\mathbf{E}\perp c$ polarization as the Γ_{5T} states of the *A* and *B* excitons. In the case of $\mathbf{E}\parallel c$ polarization, the observed peaks are attributed to the Γ_6 state of the *A* exciton and the Γ_1 state of the *B* exciton. The appearance of the dipole-forbidden Γ_6 state in the spectra can be explained as being due to the finiteness of the exciton wave vector. The finite $\mathbf{k}$ vector acts as a perturbation which mixes the Γ_6 state with the Γ_1 state of the *B* exciton. Since $\Gamma_6\times\Gamma_1$ transforms as Γ_6, this perturbation must have Γ_6 symmetry like $(k_x^2-k_y^2, 2k_xk_y)$.[6] The presence of a small uniaxial strain also can induce the appearance of the Γ_6 state through the $(\varepsilon_{xx}-\varepsilon_{yy}, 2\varepsilon_{xy})$ perturbation.

The energy separation between the peaks assigned as Γ_{5T}^A and Γ_6^A is a measure of the singlet-triplet splitting of the *A* exciton resulting from the analytical part of the spin-exchange interaction. It is found to be 0.53 ± 0.02 meV in the heteroepitaxial layer and 0.52 ± 0.04 meV in the free standing sample. These values are much smaller than the value of 2.9 meV reported by Reynolds *et al.*[14] We should mention that the PL spectrum for $\mathbf{E}\parallel c$ polarization in Ref. 14 is very similar to that we observe in the free standing sample and the peak assigned by the authors as Γ_6^A state is more likely due to the D^0X_B exciton. On the other hand, the Γ_{5T}^A-Γ_6^A splitting obtained here is slightly larger that it was previously measured in a thicker HVPE GaN layer grown on *c*-plane sapphire (120 ± 0.1 meV).[12] In this sample, however, the emission of the *A* exciton is rather broad and the exact positions of Γ_6^A and Γ_{5T}^A states were extracted by a spectral deconvo-

lution. In contrast, our samples reveals well resolved free-exciton peaks in both polarizations and the Γ_{5T}^{A}-Γ_{6}^{A} splitting can be determined directly. We believe that the discrepancy in the reported values cannot be attributed to the strain variation, because our results show almost the same singlet-triplet splitting in both the nearly strain-free sample and the biaxially compressed layer. From the spectra in Fig. 2, we can also deduce the energy splitting between the two optically active states of the *B* exciton Γ_{5}^{B} and Γ_{1}^{B}. It is found to be 0.240 ± 0.08 meV. To the best of our knowledge, the splitting of the *B* exciton in GaN was not experimentally observed up to now. Unfortunately, we are not able to obtain the Γ_{5}^{B}-Γ_{1}^{B} splitting in the free-standing sample because the emission of the *B* exciton for $\mathbf{E} \perp c$ polarization is very weak and its energy position cannot be determined precisely.

It is important to note that due to the polariton effects, the Γ_{5T}^{A}-Γ_{6}^{A} splitting obtained from the PL spectra might be considered as a lower limit of the singlet-triplet splitting of the *A* exciton. The strong coupling of the electromagnetic field with the dipole-allowed exciton states (Γ_5) give rise to mixed photon-exciton states (polaritons). The electron-hole pairs created by a nonresonant excitation relax down to the knee of the lower polariton branch (''relaxation bottleneck region'') and the emission occurs just below the energy of the Γ_{5T}^{A} exciton state. Strictly speaking the polariton emission mechanisms transforms into a transport of the coupled excitation from the depth of the crystal to the surface where only part of it is transmitted due to the additional boundary conditions.[9] As a result, the luminescence yield from the polaritons is rather low compared to that from the bound complexes. In the case of $\mathbf{E} \| c$ polarization, there is no exciton-photon coupling and a purely excitonic emission of the Γ_{6}^{A} state with a Lorentzian line shape can be observed.

To interpret quantitatively our experimental results, we follow the approach of Langer *et al.*,[23] who described the internal structure of the excitons in a strained wurtzite crystal. In GaN, the conduction band is predominantly *s*-like and the valence band is *p*-like. The three *p*-type functions and the two spin states for both the electron and the hole lead to a 12-fold degenerate exciton ground state. The exciton Hamiltonian can be written as

$$H = H_c - H_v - R + H_{\mathrm{exch}}, \tag{1}$$

where H_c and H_v are the conduction and valence and Hamiltonians, adapted to account for the strain related effect on the band extrema, *R* is the customary exciton binding energy, which is assumed to be constant, and H_{exch} describes the electron-hole exchange interaction. In the case of growth on *c*-plane sapphire, the GaN layer is under a biaxial compressive stress and there are only two nonvanishing components of the strain tensor, ε_{zz} and $\varepsilon_{xx} = \varepsilon_{yy}$. The conduction band and valence and Hamiltonians for $\mathbf{k} = 0$ are given by[5,23]

$$H_c = E_c + D_1 \varepsilon_{zz} + D_2 (\varepsilon_{xx} + \varepsilon_{yy}) \tag{2}$$

and

$$H_v = \Delta_1 L_z^2 + \Delta_2 L_z \sigma_{h,z} + \Delta_3 (L_x \sigma_{h,x} + L_y \sigma_{h,y}) + (C_1 + C_3 L_z^2)\varepsilon_{zz} + (C_2 + C_4 L_z^2)(\varepsilon_{xx} + \varepsilon_{yy}). \tag{3}$$

Here, E_c is the conduction band energy at zero strain, D_i are the conduction band deformation potentials, Δ_1 is the wurtzite crystals-field parameter, Δ_2 and Δ_3 are the spin-orbit coupling parameters along the *c* axis, L_i and $\sigma_{h,i}$ are the components of the orbital (spinless) and the spin hole moments, and C_i are the spin independent valence band deformation potentials. The spin-orbit interaction and the crystal field split the ground exciton state into three four-fold degenerate excitons (*A*, *B*, and *C*). The last term in Eq. (1) takes into account only the analytical part of the exchange interaction and is written by[24]

$$H_{\mathrm{exch}} = \frac{1}{2}\gamma(1 - \sigma_e \sigma_h), \tag{4}$$

where γ is the isotropic exchange interaction constant between the hole and electron spins and σ_e and σ_h denote the vector operators whose components are the Pauli spin matrices of the electron and the hole, respectively. This part of the Hamiltonian accounts for the splitting of the degenerate *A*, *B*, and *C* excitons and the mixing of their oscillator strengths. H_{exch} contributes only to the spin-singlet states and keeps the energy of the spin-triplet states unchanged. The exchange constant is defined as $\gamma = \Omega |\phi_{1s}(0)|^2 J$, where Ω is the volume of the unit cell, $\phi_{1s}(\mathbf{r}_e - \mathbf{r}_h)$ is the $1s$ hydrogenlike function which describes the relative motion of electron and hole, and *J* is the atomiclike exchange energy.[25] Strictly speaking this definition holds only for a cubic crystal and is more questionable in a wurtzite crystal where the ground state is not exactly described by the $1s$ state. Nevertheless, a formalism for *ab initio* calculation of γ in II-VI compounds has been developed by Rohner.[26] Applying the same approach, Gil *et al.* estimated $\gamma = 2$ meV in GaN.[5] In our consideration, the exchange interaction constant will be treated as an adjustable parameter and its value will be extracted from the experimentally obtained energy separation between the exciton states.

For the analysis of the exciton fine structure, we choose a set of basis wave functions which are classified by the symmetry of the exciton states.[5] Thus, the 12×12 Hamiltonian matrix can be decomposed into two 6×6 matrices, one for the states of Γ_5 symmetry and another one for the Γ_1, Γ_2, and Γ_6 states. The energies of the 12 exciton states are obtained by diagonalization of these matrices of various levels of the stress. The components of the strain tensor in Eqs. (2) and (3) are related to the in-plane stress τ_{xx} by[27]

$$\varepsilon_{xx} = -\left(C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}} \right)^{-1} \tau_{xx} \tag{5}$$

and

$$\varepsilon_{zz} = \frac{2C_{13}}{C_{33}} \left(C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}} \right)^{-1} \tau_{xx}, \tag{6}$$

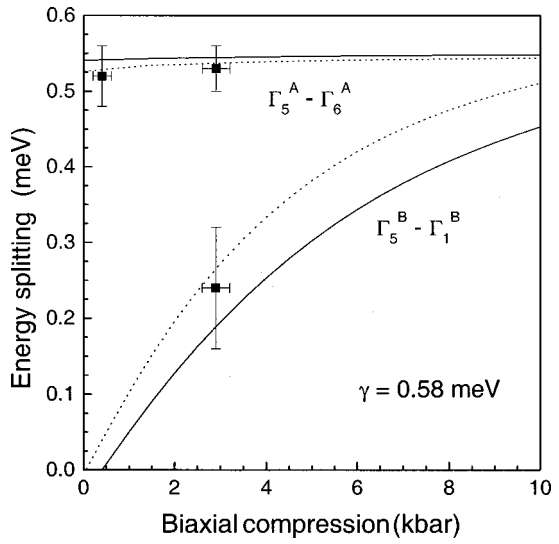

FIG. 5. Stress dependence of the energy splitting Γ_5^A-Γ_6^A and Γ_5^B-Γ_1^B calculated with parameters $\Delta_1=10$ meV, $\Delta_2=6.2$ meV, $\Delta_3=5.5$ meV, and $C_3=4.91$ eV (Ref. 29) (solid lines) and $\Delta_1=10$ meV, $\Delta_2=5.5$ meV, $\Delta_3=6.0$ meV, and $C_3=7.2$ eV (Ref. 30) (dotted lines). The squares represent the experimentally obtained values.

where for the stiffness coefficients we use $C_{11}=365$ GPa, $C_{12}=135$ GPa, $C_{13}=114$ GPa, and C_{33} 381 GPa.[28] To calculate the stress evolution of the exciton states, the values of the six deformation potentials D_i and C_i are also required. Since we are interested in the splitting between exciton states and not in their absolute energies, the number of the deformation potentials needed is reduced to two, C_3 and C_4, or even to one if a quasicubic approximation is used, i.e., $C_3=-2C_4$.[29]

We calculate the splitting between the exciton states as a function of the biaxial stress with the following valence band parameters: $\Delta_1=10$ meV, $\Delta_2=6.2$ meV, $\Delta_3=5.5$ meV, and $C_3=4.91$ eV.[29] The exchange interaction constant γ is adjusted by an iterative procedure until the calculated values of Γ_5^A-Γ_6^A and Γ_5^B-Γ_1^B match the measured ones. The best fit is obtained for $\gamma=0.58\pm0.05$ meV. The stress variation of the energy separations Γ_5^A-Γ_6^A and Γ_5^B-Γ_1^B calculated with this value of γ is shown in Fig. 5. The singlet-triplet splitting Γ_5^A-Γ_6^A exhibits a weak dependence on the stress which is consistent with the experimental results. The Γ_5^A-Γ_6^A increases by only 3% in the stress region from 0 to 10 kbar. On the other hand, the Γ_5^B-Γ_1^B splitting is found to be very sensitive to the stress. It is interesting that the calculations yield a negative value for Γ_5^B-Γ_1^B at zero stress. Such an inverse ordering of Γ_1^B and Γ_5^B states has also been observed in unstrained CdS.[24] The anticrossing of Γ_1^B and Γ_5^B states in GaN was predicted to take place for a tensile stress ($\tau_{xx}<0$) when a larger exchange interaction constant was used ($\gamma=2$ meV).[5] The splitting between the two optically active states of the C exciton (not shown here) exhibits a stress dependence similar to that for the B exciton, but with a zero stress value of 0.5 meV. For a compressive stress, the state Γ_1^C is always at higher energy than the Γ_5^C state. To test the sensitivity of the theoretical results to the input parameters, we repeat the calculation with another set of parameters, namely, $\Delta_1=10$ meV, $\Delta_2=5.5$ meV, $\Delta_3=6.0$ meV, and $C_3=7.2$ meV.[30] The results are shown in Fig. 5 with doted lines. The change of parameters practically do not influence the singlet-triplet splitting of the A exciton. However, the new parameters yield a larger Γ_5^B-Γ_1^B splitting and apparently a better agreement with the experimental value is found. The almost identical stress evolution of the Γ_1^B-Γ_5^B and Γ_5^B-Γ_5^A in both cases suggests that the main difference comes from the different spin-orbit parameters.

In spite of an uncertainty of the valence band parameters in GaN, the theoretical calculations describe rather well our experimental results for the energy splitting of the exciton states. Moreover, the determined exchange interaction constant is in a nice agreement with the value $\gamma=0.6\pm0.1$ meV estimated from the polarized reflectance measurements for $\mathbf{k}\|c$ configuration in a thin GaN layer grown on a-plane sapphire.[31] As it was pointed out in Ref. 31, this value is consistent with the expected exponential dependence of γ on the interatomic distance in the Ga-based III-V compounds. The lower exchange interaction constants in GaN, with respect to the values obtained for II-VI compounds can be explained by the more covalent character of the chemical bonds.

Finally, we would like to point out that the splitting between exciton states we obtained in a GaN layer grown on a-plane sapphire is large, namely, Γ_5^A-$\Gamma_6^A=0.94\pm0.03$ meV and Γ_5^B-$\Gamma_1^B=0.69\pm0.1$ meV.[32] The explanation of the observed difference can be based on the fact that GaN layers grown on a-plane sapphire exhibits an anisoptropic in-plane compression due to the different thermal expansion coefficients of the sapphire in directions parallel and perpendicular to the c axis. This anisotropy acts as an uniaxial stress and leads to the reduction of the crystal point group from the hexagonal to the orthorhombic one.[31] As a result, the twofold degeneracy of the Γ_5 state is lifted even at $\mathbf{k}\|c$ and two transverse excitons with a dipole momentum polarized parallel to the x and y axis are observed. Accordingly, the energy position of the Γ_{5T}^A and Γ_{5T}^B states for $\mathbf{k}\perp c$, $\mathbf{E}\perp c$ configuration depends on the angle between the wave vector and the direction of the uniaxial stress. The detailed analysis of the internal exciton structure in GaN grown on a-plane sapphire as well as the dependence of the energy splitting on the wave vector orientation is a subject of a separate study.

V. CONCLUSIONS

We have used polarized photoluminescence spectroscopy to study the internal exciton structure in GaN. A noticeable difference between the free-exciton emission spectra polarized perpendicular and parallel to the c axis of the crystal was found. The observed emission from the spin-triplet state of the A exciton allowed us to determined directly the singlet-triplet splitting Γ_5^A-Γ_6^A in GaN. Almost the same splitting was measured in the heteroepitaxial layer and in the free-standing, nearly strain-free sample. In the strained sample, we were able to observe the energy splitting between the two singlet states of the B exciton. A theoretical model-

ling of the exciton structure was also performed, and the splitting between the exciton states was calculated as a function of the stress in biaxialy compressed layers. We found that the singlet-triplet splitting Γ_5^A-Γ_6^A weakly depends on the stress, while the splitting between the Γ_5 and Γ_1 states of the *B* exciton increases with the increase of the stress. By fitting the calculated energy splitting to the experimentally obtained values, the exchange interaction constant in GaN was determined to be $\gamma = 0.58 \pm 0.05$ meV.

ACKNOWLEDGMENTS

The authors would like to thank to B. Gil for fruitful discussions and to F. Karlsson for the technical assistance in the experiments.

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