FINE STRUCTURE AND MAGNETOOPTICS OF EXCITONIC LEVELS IN WURTZITE GaN

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ABSTRACT

We present a comprehensive study of the direct photoluminescence from excitonic states in GaN using polarization-dependent and magnetooptical measurements in fields up to 15 T. We measure and identify fine-structure splittings in the states n=1 and n=2 of the A-exciton. The splitting between the energy levels of longitudinal and transverse states in the A-exciton is 0.96 meV. Emission from the spin triplet exciton in the state n=1 is observed. We also identify emissions from three sublevels of the state n=2 of the A-exciton. From the analysis of our data we obtain the effective-mass parameters of electrons and holes, g-values and the Rydberg energy of the A-exciton.

INTRODUCTION

The investigation of excitons in semiconductors has been an important key to the understanding of the electronic structure and the optical properties of these materials. The hydrogen-like spectrum of excitonic energy levels detected in optical experiments is very sensitive to the values of the effective masses of electrons and holes, the crystal field and its symmetry, and many other internal and external influences like, for instance, the exchange interaction or a strain field [1]. With the advances in the growth technology of the group-III nitrides GaN, InN and AlN, as well as their ternary alloys this group of wide-gap semiconductors with wurtzite crystal structure has become technologically quite important. Their optical properties and electronic structure, however, are only poorly understood. Data in the literature on excitonic fine structure splittings [2,3,4] and effective masses of charge carriers [5-11] of GaN exhibit some scatter or are still incomplete. Thus, closing the gap in the knowledge of these materials has become an urgent matter.

EXPERIMENTAL

The experimental approach taken in this work is the careful analysis of the direct, i.e., zero-phonon exciton emission in low-temperature photoluminescence spectra from high-quality samples. To be able to distinguish between luminescence polarized parallel and perpendicular to the c-axis we detected only light from a side face of the epilayers which were 300 and 400 µm thick. The samples used for this study are high-quality GaN epilayers grown on (0001) sapphire by hydride vapor phase epitaxy (HVPE).

Photoluminescence was performed under continuous-wave (cw) excitation at 325 nm using a HeCd laser. The sample was mounted in an immersion cryostat for zero-field experiments at 2 K. For magnetoluminescence experiments in Faraday configuration a 15 T split-coil magnet was employed. To obtain spectral positions with as high an accuracy as

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possible from the PL measurements we performed lineshape fits to the measured spectra using only symmetric Gaussian and Voigt line shapes for the individual peaks. For each spectrum the complete range of free-exciton luminescences was fitted in order to obtain the highest possible accuracy in energy positions.

RESULTS

The State n=1 of the A-Exciton

Figure 1 displays the polarized low-temperature emission in the range of the n=1 state of the A-exciton observed from a side face of a free-standing 300 μm thick sample. In Figure 1 (a) the detected light is polarized perpendicular to the c-axis, in Figure 1 (b) parallel. Both spectra are well fitted by a sum of two peaks and the underground from the neighboring weak B-exciton emission on the low-energy side and the stronger donor-bound B-exciton (D^0,X_B) on the low-energy side. While the high-energy peak is seen at the same energy of 3.48000 eV in both polarizations within our experimental accuracy a difference in the low-energy peak positions is observed between the perpendicular and parallel polarizations of Figures 1 (a) and (b), respectively. In perpendicular polarization 3.47904 eV is the measured peak position while in parallel polarization we find 3.47892 eV. We identify the latter value with that of the spin triplet state (Γ_6) of the A-exciton and the former with that of the transversal branch of the spin singlet state (Γ_{5T}). Thus, the energy difference of 120±100 μeV between the peaks corresponds to the splitting of these states caused by the exchange interaction between electron and hole in the Γ_{5T} state. We assign the peak energy of 3.48000 eV seen in both spectra to the position of the longitudinal branch of the spin singlet exciton (Γ_{5L}). This gives a value for the LT splitting of the Γ_5 state of 0.96±0.10 meV. This value is in very good agreement with an analysis of the reflection data [12] using additonal boundary conditions given by Pekar.

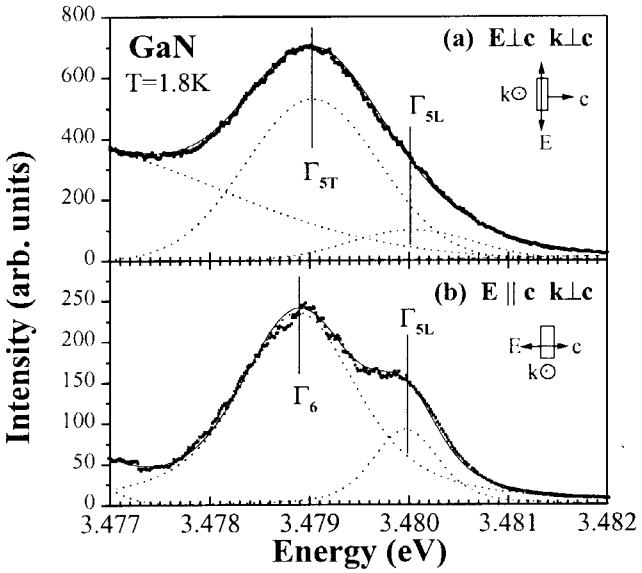

Figure 1: Polarized low-temperature photoluminescence spectra taken from a side face of a 300 μm thick HVPE sample.

The dependence of the peak positions on the magnetic field is shown in Figure 2. For H||c the splitting expected from theory is resolved here for the first time in contradiction to earlier work by Skromme et al. [3]. The analysis of the energy differences reveals that the twofold splittings of the Γ_5 and Γ_6 states each follow the expected linear behavior. Thus, the g-values of the electron and the hole for this configuration can be determined. They amount to $g_e^{\parallel} = 2.3\pm0.2$ and $g_h^{\parallel} = -1.3\pm0.2$. The diamagnetic shift of the Γ_6 states is 4.0±0.3 μeV/T^2. For the longitudinal and transverse Γ_5 states no diamagnetic shift can be extracted from the

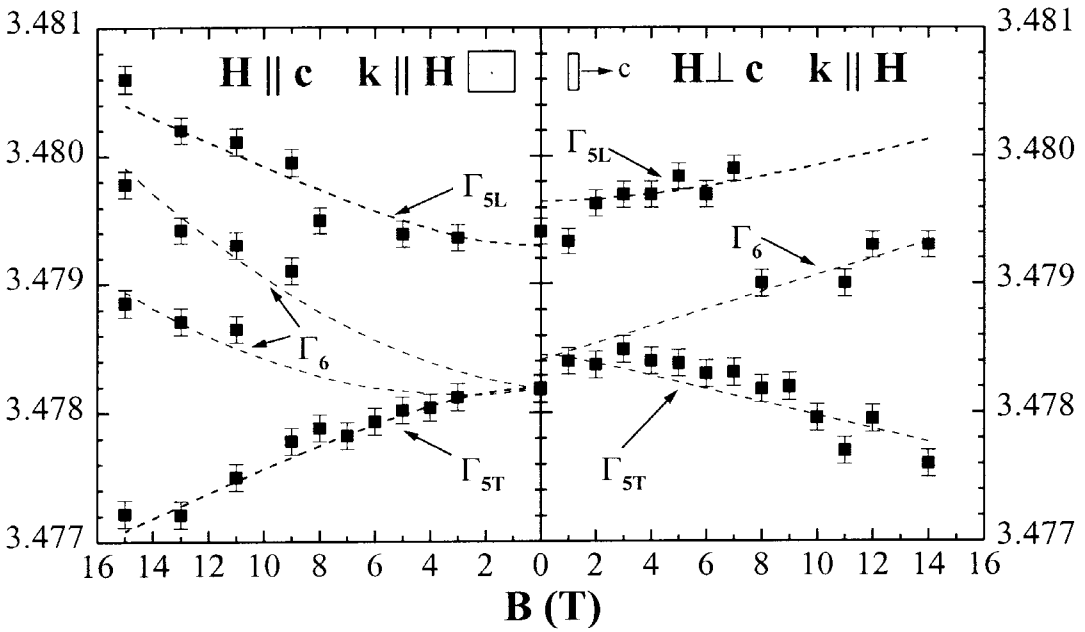

Figure 2: Dependence of the peak energies of the state n = 1 of the A-exciton on magnetic fields parallel and perpendicular to the c-axis.

obtained data in both configurations which we ascribe to an additional mixing of these states induced by second-order magnetic-field effects. The observation of the mixing of these states is strong evidence for the correctness of our assignment of the respective emission lines and the value of the LT-splitting determined in the zero-field PL spectra.

For $H \perp c$ one expects a mixing between Γ_5 and Γ_6 giving rise to a linear splitting superimposed by the twofold spin splitting of each state. Due to the weakness of the emissions on the high-energy side of the Γ_{5T} in this configuration we can follow the Γ_{5L} only up to 8 T. From here on a weak shoulder at lower energies due to the Γ_6 can be observed without, however, allowing to resolve a splitting in this state. From the splitting of the Γ_{5T} and Γ_6 states at higher fields the conduction band g-value is determined for this configuration and amounts to 2.0±0.2 in good agreement with the results of other studies. We list the determined parameters in table 1 at the end of this paper.

The value of 0.96 meV for the LT splitting in GaN is smaller than that in CdS (2.1 meV) or CdSe (1.6 meV) [13]. This accounts for much of the different magnetooptical of this state seen in Figs. 3 and 4 in comparison to these materials. In CdS the interaction of the two $1S\Gamma_5$ components, especially in a magnetic field $\boldsymbol{H} \parallel \boldsymbol{c}$, is not observed due to their large splitting and, thus, the quenching of the respective magnetic interaction terms. In GaN the LT splitting is small and the interaction is detected by the shift of the $1S\Gamma_{5T}$ to lower energies and the $1S\Gamma_{5L}$ to higher energies. Skromme *et al.* observed in magnetoluminescence experiments only a slight broadening of the luminescence from the state n=1 of the A-exciton in GaN using the configuration $\boldsymbol{H} \parallel \boldsymbol{c}$, $\boldsymbol{k} \parallel \boldsymbol{H}$. We believe that our observation of splittings is due to smaller linewidths in our sample.

The State n=2 of the A-Exciton

In Figure 3 low-temperature PL measurements are shown in the spectral range of the n=2 state of the A exciton, polarized perpendicular (a) and parallel to the c-axis (b). A total of four

lines is observed. The two lower-energy lines at 3.49607, 3.49420 eV exhibit a strong polarization contrast while the intensity of the high-energy line at 3.49864 eV is only weakly dependent on the detected polarization. We conclude that according to the selection rules the former luminescences are emitted from Γ_5 states and that latter is emitted from a superposition of two or more degenerate Γ_5 and Γ_1 states. The weak line at 3.49724 eV also appears stronger in perpendicular polarization. In this spectral range the states n=2 of both, A- and B-excitons can be expected. We give our assignments at this point already to keep the presentation clear. They are based on the polarized zero-field spectra presented here and the magnetooptical data presented below. The two low-energy lines are due to the $2P_z$ and 2S envelopes of the A-exciton. The high-energy line at 3.49864 eV is due to the 2Px,y state of the A-exciton. The weak line at 3.49724 eV is tentatively assigned to the 2S (Γ_5) state of the B-exciton.

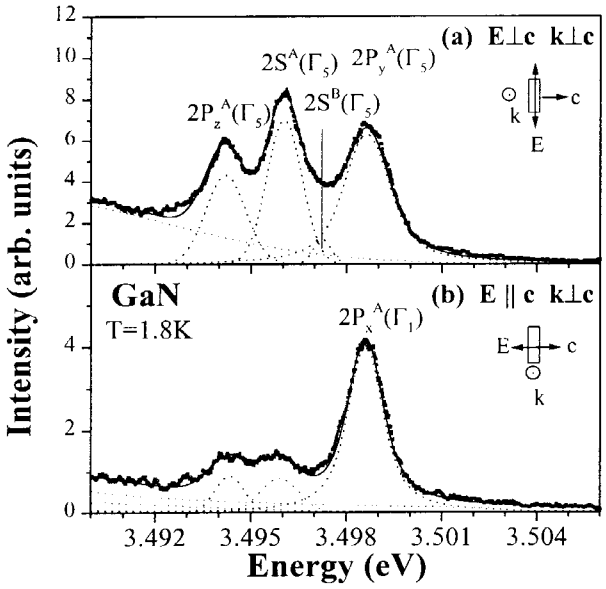

Figure 3: Polarized photoluminescence spectra in the range of the n = 2 state of the A-Exciton.

For our magnetooptical measurements on the state n=2 we also employed the configuration H⊥c (oriented along the x-axis) in contrast to the work of Skromme *et al.* [3]. In this configuration there is no longer any good quantum number allowing an unambiguous identification of the observed states due to their characteristic diamagnetic shifts and splittings.To evaluate the obtained data we used the theory developed by Hopfield and Thomas for the case of CdS [14], modified only by the omission of a linear interaction term between the $2P_y$ and $2P_z$ states. Our results presented above demonstrate that in GaN their zero-field splitting (4.4 meV) is much larger than in CdS (0.5 meV), and thus quenches their interaction due to the magnetic field. We obtained a good agreement using the parameters listed summarized in table 1 at the end of this paper. The exciton Bohr radius used was 27.5 Å. For the observed S-states we performed second-order polynomial fits to obtain the linear and quadratic shift characteristics. The 2S state exhibits no resolvable linear shift, the quadratic diamagnetic shift is -8±2 $\mu eV/T^2$. The linear shift parameter of $2S^B$ is 80±20 $\mu eV/T$, the diamagnetic shift is 3.8±1.5 $\mu eV/T^2$. The g-values obtained are largely in agreement with results obtained by other groups [15].The absolute value of the g-value determined here for the A-valence band parallel to the c-axis (-1.3) is larger than that estimated previously on the basis of magnetoluminescence measurements on the donor-bound exciton [16].While the qualitative appearance of the spectra observed by us is similar to that of Skromme et al. [3] we differ from their interpretation, which included for instance also assignments to the state n=3 of the A-exciton. The analysis of their data was carried out on the basis of a rather crude model for the hydrogen atom in a magnetic field, which seems too simple to hold for the situation of an exciton in an anisotropic crystal such as GaN. We believe that our assignments were made on a better experimental and theoretical [14] basis.

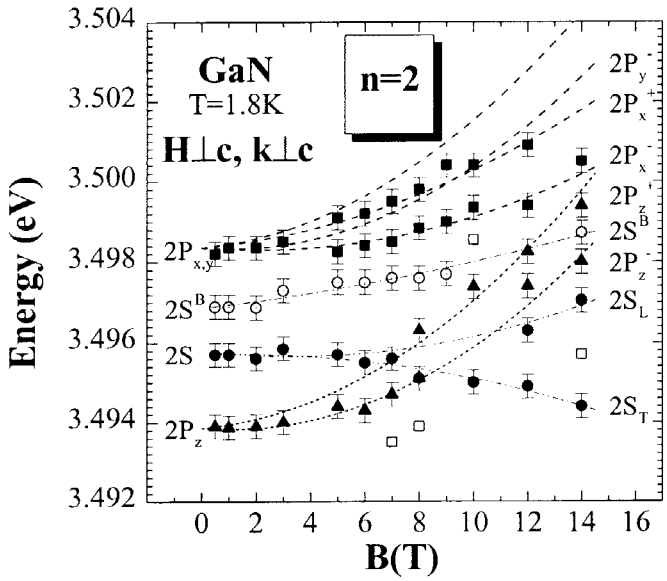

Figure 4: Dependence of the energy positions of the states n=2 of the A-Exciton on magnetic field. For the P-states the fits are based on a calculation by Hopfield and Thomas[14].

From our analysis a set of basic parameters was obtained containing the effective masses of the conduction and A-valence bands, and the dielectric constants of GaN. The calculated magntic field dependence of the 2P states is very sensitive to a change in the dielectic constants. The values used for the fit $\varepsilon_{\parallel} = 10$ $\varepsilon_{\perp} = 9.1$ are in very good agreement with those obtained ($\varepsilon_{\parallel} = 10.1$, $\varepsilon_{\perp} = 9.28$) using polarized Raman spectroscopy [17]. Concerning the effective mass of the electron in the conduction band there is agreement in the literature and our value of 0.2 confirms most of the previously published results. There is some scatter in the literature in the values of the effective hole masses. For $m_A^{\perp}$ only theoretical data have been published to the best of our knowledge. Different authors obtained 1.65 [5] and 0.33 [6]. Our value of 0.9 does not agree with either of these results. For $m_A^{\parallel}$ both theoretical and experimental data can be found, the former being 2.03 [6]or 1.1 [5], the latter 0.54 [9], 0.8[7], 1 [10,11], or 2.2 [8]. Our value of 1.3 is close to that used by Cunningham et al. [11] to fit the Burstein shift in their luminescence spectra of highly n-doped GaN. The value of $m_A^{\perp}$ determined here has some uncertainty since a change by ±0.3 of this parameter does not strongly influence the quality of the fit. However, there is no doubt that $m_A^{\parallel} > m_A^{\perp}$ also from the zero-field splitting between the states $2P_z$ and $2P_{xy}$. It would otherwise have the opposite sign. The observed value of the zero-field splitting is much larger than expected for the given anisotropy. This is evidence for a strong mixing between the excited states of A- and B-excitons, which are expected in the same energy range.

The knowledge of the effective mass parameters allows to calculate the exciton Rydberg energy, which amounts to 26.9 meV. It differs from the exciton binding energy of 23.8 meV of the state n = 1 which strictly speaking can only be determined knowing the exact value of the band gap energy. The difference is caused by interactions acting only on the state n = 1 since for this state effective-mass theory has only limited validity due to its large distance from the continuum [18].

CONCLUSION

The thorough analysis of polarized photoluminescence and magnetoluminescence spectra of excitonic states allows to deduce fine structure splittings, g-values, effective mass parameters. They are listed in table 1. Using these values and the dielectric constants $\varepsilon_{\parallel} = 10$ $\varepsilon_{\perp} = 9.1$ the exciton Rydberg energy for GaN was calculated and amounts to 26.9 meV. It

differs from the bindig energy of the state n = 1 which is 23.8 meV in quasi-bulk sample investigated.

Valence band			
$m_A^{\perp}$	$m_A^{\parallel}$	m_A	$g_A^{\parallel}$
0.9±0.3	1.3±0.2	1.0	-1.3±0.2
Conduction band			
$m^{\perp}$	$m^{\parallel}$	$g^{\parallel}$	$g^{\perp}$
0.2±0.03	0.2±0.03	2.3±0.2	2.0±0.2

Table 1: Effective mass parameters and g-values of GaN.

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