RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 56, NUMBER 12 15 SEPTEMBER 1997-II

Zeeman splittings of excitonic transitions at the Γ point in wurtzite GaN: A magnetoreflectance investigation

J. Campo, M. Julier, D. Coquillat, J. P. Lascaray, D. Scalbert, and O. Briot
Groupe d'Etudes des Semiconducteurs, c.c. 074, URA 357 CNRS, Université Montpellier II, place Eugène Bataillon,
34095 Montpellier CEDEX 5, France

(Received 17 March 1997)

Wurtzite GaN on (0001) sapphire is studied by means of reflectance and magnetocircular dichroism up to 5.5 T at 2 K. This very powerful technique allows us to determine the Zeeman splittings to be about 0.05 meV/T for the X_A and X_C excitons and almost zero for the X_B exciton. Reflectance and dichroism are interpreted with a model of Gaussian dispersion of the excitonic energies and are in excellent agreement with previously proposed band-edge models. [S0163-1829(97)51036-8]

I. INTRODUCTION

The recent improvements in gallium nitride growth techniques and the success in producing both p and n types have led to an increasing interest in this material, due to its potential applications for optoelectronic devices operating in the short-wavelength spectral region[1] and capable of operation up to about 500 °C.

GaN grown onto (0001) sapphire substrates is a direct wide band-gap semiconductor with wurtzite structure. The energy-gap value has been shown to be 3.50 eV at low temperatures[2] (3.4 eV at 300 K). The valence-band structure at the Brillouin zone center can be derived from the irreducible representations of C_{6v} at the Γ point. The p-type valence band is split off by crystal-field and spin-orbit effects into strongly coupled and doubly degenerate Γ_9, upper Γ_7, and lower Γ_7 levels.[3] These bands are labeled as A, B, and C, respectively. In the presence of an external magnetic field, their degeneracy is lifted, and their mixing gives rise to new eigenstates of the system and peculiar selection rules.[4] A magnetic field will also split off the doubly degenerate s-type conduction band, labeled as S, without modifying its eigenvectors. Due to the crystal symmetry, the bands are characterized by the c-axis component of their total angular momentum: $J_z = \pm\frac{1}{2}$ for the S, B, and C bands, and $J_z = \pm\frac{3}{2}$ for the A band.

Magnetocircular dichroism is a kind of modulation spectroscopy that has proven to be very powerful in understanding the electronic properties of semiconductors.[5,6] In a nonmagnetic semiconductor, such as GaN, the Zeeman splitting of the excitons is very little ($\approx$0.05 meV/T) and it is impossible to resolve it directly at practical magnetic fields. However, each energy-split transition has its own characteristic polarization.[7] Hence, based on magnetocircular dichroism measurements, we are able to determine the fine structure of the free exciton states[8] in GaN.

The purpose of the present paper is to determine from magnetoreflectance measurements the energy and oscillator strengths of the excitonic transitions for heavy holes X_A and light holes $X_{B,C}$, the crystal field Δ_1, and spin-orbit parameters Δ_2, Δ_3 of GaN grown onto (0001) sapphire. Experimental results of Zeeman splitting for heavy and light hole excitonic transitions are also obtained using magnetocircular dichroism, and corresponding effective g values are calculated. Zeeman splitting for the bands A, B, and C are determined.

The paper is organized in the following way: in Sec. II, the experimental setup will be briefly described. In Sec. III, a theoretical primer will be given, dedicated to the physics of wurtzite-type semiconductors (in the first part) and more specifically to the reflectance and magnetocircular dichroism techniques (in the second part). In Sec. IV, experimental results will be exposed and discussed.

II. EXPERIMENTAL SETUP

The GaN layer studied in this paper was a 4-μm-thick epilayer grown in a low-pressure (76 Torr) ASM 12 horizontal MOVPE reactor at 985 °C, under hydrogen flow. The precursors were ammoniac and triethylgallium, and the substrate was (0001) sapphire. A thin GaN buffer layer was grown at low temperature ($\approx$600 °C) on the nitrated substrate before the epitaxy of GaN began. This is a standard procedure used to obtain GaN epilayers and will be described elsewhere.[9]

Magnetoreflectance measurements were performed in the Faraday configuration. The sample was placed in a magneto-optical cryostat equipped with a split superconducting coil for a magnetic field up to 5.5 T. The measurements were carried out at 2 K. The source was a tungsten filament lamp. The reflected signal was analyzed using a double synchronous detection technique. A first lock-in tuned to a chopper, with a frequency of 23 Hz, measured the $I^+ + I^-$ reflectance signal while at the same time a second one, operating at the frequency (50 kHz) of a Hinds photoelastic modulator, measured the magnetocircular dichroism signal $I^+ - I^-$. The description of the magnetocircular-dichroism technique is beyond the scope of this paper; details have been previously given in Ref. 5. This measurement allows one to determine absolute values of the circular polarization rate $P = (I^+ - I^-)/(I^+ + I^-)$ and reflectance $R = (I^+ + I^-)/2$ in arbitrary units. The measurements were done typically at 1 Å intervals.

0163-1829/97/56(12)/7108(4)/$10.00

III. THEORETICAL BACKGROUND

A. Near-gap bands at the Γ point in wurtzite semiconductors

The Hamiltonian near the band edge, following Kane's model,[10] can be written as

$$H=H_0+\frac{\hbar^2k^2}{2m_0}+\frac{\hbar}{m_0}\,\mathbf{k}\cdot\mathbf{p}+H_{so}, \qquad (1)$$

where $H_0=\frac{p^2}{2m_0}+V(\mathbf{r})$ and $H_{so}=\frac{\hbar}{4m_0^2c^2}\,(\nabla V\times p)\sigma$.

$V(\mathbf{r})$ is the periodic potential, H_{so} represents the spin-orbit interaction, and σ are the Pauli matrices. For the valence bands near the Γ point, we have chosen the following basis (written as $|L,L_z,S_z\rangle$): $\{|1,1,\uparrow\rangle,|1,1,\downarrow\rangle,|1,0,\uparrow\rangle,|1,-1,\downarrow\rangle,|1,-1,\uparrow\rangle,|1,0,\downarrow\rangle\}$, with orbital parts given by $|1,0\rangle=|Z\rangle$ and $|1,\pm1\rangle=(\mp|X\rangle-i|Y\rangle)2^{-1/2}$ where $|X\rangle$, $|Y\rangle$, and $|Z\rangle$ transform like P_x, P_y, and P_z atomic wave functions at $\mathbf{k}=\mathbf{0}$. In this basis, the Hamiltonian (1) for valence-band edges writes

$$H=\begin{pmatrix} H_3 & 0\\ 0 & H_3\end{pmatrix},\quad \text{with } H_3=\begin{pmatrix} 0 & 0 & 0\\ 0 & -2\Delta_2 & \sqrt{2}\Delta_3\\ 0 & \sqrt{2}\Delta_3 & -\Delta_1-\Delta_2\end{pmatrix}, \qquad (2)$$

where Δ_1 is the crystal-field energy, and Δ_2 and Δ_3 are the spin-orbit coupling parameters, respectively, parallel and perpendicular to the c axis. The energy of the A band has been taken as a reference. Diagonalizing the Hamiltonian matrix (2), we obtain the following eigensystem:

Band	J_z	Eigenvectors	Energy at zero field
A	$+\frac{3}{2}$	$\|1,1,\uparrow\rangle$	0
	$-\frac{3}{2}$	$\|1,-1,\downarrow\rangle$	
B	$+\frac{1}{2}$	$a_+\|1,1,\downarrow\rangle+\sqrt{1-a_+^2}\|1,0,\uparrow\rangle$	$-\frac{\Delta_1+3\Delta_2}{2}+\sqrt{\left(\frac{\Delta_1-\Delta_2}{2}\right)^2+2\Delta_3^2}$
	$-\frac{1}{2}$	$a_-\|1,-1,\uparrow\rangle+\sqrt{1-a_-^2}\|1,0,\downarrow\rangle$	
C	$+\frac{1}{2}$	$\sqrt{1-a_+^2}\|1,1,\downarrow\rangle-a_+\|1,0,\uparrow\rangle$	$-\frac{\Delta_1+3\Delta_2}{2}-\sqrt{\left(\frac{\Delta_1-\Delta_2}{2}\right)^2+2\Delta_3^2}$
	$-\frac{1}{2}$	$\sqrt{1-a_-^2}\|1,-1,\uparrow\rangle-a_-\|1,0,\downarrow\rangle$	

Without a magnetic field, a_+ and a_- are equal and given by the formulas

$$a_+=a_-=a=\frac{1}{x\sqrt{1/x^2+1}},\quad \text{where}$$

$$x=\frac{-(\Delta_1-\Delta_2)+\sqrt{(\Delta_1-\Delta_2)^2+8\Delta_3^2}}{2\sqrt{2}\Delta_3}.$$

Because of the selection rules $\Delta L_z=\pm1$ (in $\sigma^\pm$ polarization, respectively), the oscillator strengths are given by: $\alpha_B=a^2\alpha_A$ and $\alpha_C=(1-a^2)\alpha_A$.

So, the oscillator strengths α_A of the transition from the A band is the sum of those from the B and C bands, α_B and α_C. In a magnetic field, the degeneracy between a_+ and a_- is lifted, leading to a slight dependence of α_B and α_C upon the polarization. These calculations for wurtzite semiconductors are detailed, for example, in Refs. 11 and 12.

The presence of a magnetic field along the c axis lifts the degeneracy of all the bands, giving rise to a tiny symmetric splitting ΔE_S for the conduction band, and $\Delta E_{A,B,C}$ for the valence bands where each ΔE_i is defined as $\Delta E_i=E_i(+J)-E_i(-J)$. Due to the selection rules in the Faraday configuration, we only have access to the splittings $\delta E_{A,B,C}$ of the excitonic transitions, i.e., to particular combinations of the band splittings: $\delta E_A=\Delta E_A-\Delta E_S$, $\delta E_B=\Delta E_B+\Delta E_S$, $\delta E_C=\Delta E_C+\Delta E_S$. It has been proved that in the presence of a magnetic field the exciton splittings can be taken as equal to the splittings of the band to band transitions.[13,14]

B. Reflectance and magnetocircular dichroism

The polarization rate induced by a magnetic field is straightforwardly related to the logarithmic derivative of the reflectance spectrum,[6] if a unique transition exists. That is,

$$P=\frac{R^+-R^-}{R^++R^-}\cong\frac{\delta R}{2R}=\frac{\delta E(dR/dE)}{2R}=\frac{1}{2}\,\frac{d\ \ln R}{dE}\ \delta E,$$

where δE is the splitting of the exciton and the + and − superscripts stand for the σ_+ and σ_- polarizations of light.[5] In this case, the Zeeman splitting of the excitonic transition is very easily calculated from the reflectance and polarization spectra.

However, when several excitonic transitions are quite close (in our case, X_A to X_B) and their splittings in the magnetic field are different, we cannot use the method described in the latter paragraph to calculate the Zeeman splittings. This is due to the fact that the reflectance coefficient is not simply given by the sum of three reflectance structures. In this paper, we then determine the reflectance and the polarization rate directly from the dielectric constant $\varepsilon^\pm$ for each polarization of light.

In order to calculate $\varepsilon^\pm$ in GaN, we consider three excitonic transitions labeled as X_A, X_B, and X_C, each one described by three parameters: the transition energy $E_0^\pm$ (without a magnetic field, one has $E_0^+=E_0^-\equiv E_0$), the oscillator strength $\alpha^\pm$, and the broadening factor Γ. This broadening factor is mainly due to a distribution of the band-gap energy over the surface of the sample, which is very unhomogeneous. We then assumed a Gaussian rather than a Lorentzian line shape.[15] In this case, the calculated dielectric constant is

$$\varepsilon^\pm(E)=\varepsilon_\infty+\sum_{j=A}^{C}4\pi\alpha_j^\pm\left(-\frac{2x_j}{\Gamma_j}\,\Phi\left(\frac{1}{2},\frac{3}{2},2x_j^2\right)+i\sqrt{\frac{\pi}{2}\frac{1}{\Gamma_j}}\right)\exp(-2x_j^2),$$

where $x_j=(E-E_{0,j}^{\ \pm}-\hbar^2k^2/2M_j)/\Gamma_j$. In this formula, $\Phi(\alpha,\gamma,z)$ is the degenerate hypergeometric function. The spatial dispersion term, $\hbar^2k^2/2M_i$, was calculated to be negligible in this case, and will therefore be disregarded. The background dielectric constant, ε_∞, was taken to be 9.5.[1]

To take into account the effect of the magnetic field in the dielectric constant, we have introduced a splitting parameter δE_i for each excitonic transition, defined as $\delta E_i=E_{0,i}^{\ +}-E_{0,i}^{\ -}$. Therefore, $E_{0,i}^{\ \pm}=E_{0,i}\pm\delta E_i/2$.

The perturbative effect of the magnetic field upon the oscillator strengths, illustrated by the fact that $a_+ \neq a_-$, is implemented by a new parameter $P_{BC/A}$, the oscillator strength polarization rate, defined as $P_{BC/A} = (\alpha_B^+ - \alpha_B^-)/\alpha_A = -(\alpha_C^+ - \alpha_C^-)/\alpha_A$.

The reflectance $R^\pm$ was calculated with the assumption that the sample is coated with a so-called *dead layer*, mainly due to the excitons being absent from a top layer of a thickness of the order of their Bohr radius. The exact value of this thickness is not critical to the final value of the parameters to be adjusted. We took a thickness $l_d = 60$ Å, and a dielectric constant ε_d equal to the background constant.[3]

IV. RESULTS AND DISCUSSION

Reflectance and magnetocircular dichroism measurements have been done at several magnetic fields, ranging between 0 and 5.5 T, and at a temperature of 2 K. As an example, we present reflectance [Fig. 1(b)] and dichroism [Fig. 1(a)] spectra at 5.5 T. On the reflectance spectrum we can clearly distinguish three structures corresponding to the three excitons X_A, X_B, and X_C. The X_A and X_C excitons also clearly appear on the dichroism signal at the position of the maximum slope of the reflectance structures. The X_B exciton, on the other hand, does not appear in the same way. That is, the maximum in its dichroism signal does not appear at the inflection point of its reflectance structure. We attribute this to the polarization of the oscillator strengths induced by the high magnetic field. Furthermore, its dichroism signal is smaller than that for the other excitons. This will be explained by its near-zero splitting. The low-energy limit shows interference fringes appearing because the sample turns transparent. Our assignment of X_A, X_B, and X_C excitons agrees well with the natural order of the sequence of levels Γ_9, Γ_7, and Γ_7, also seen in wurtzite ZnS.

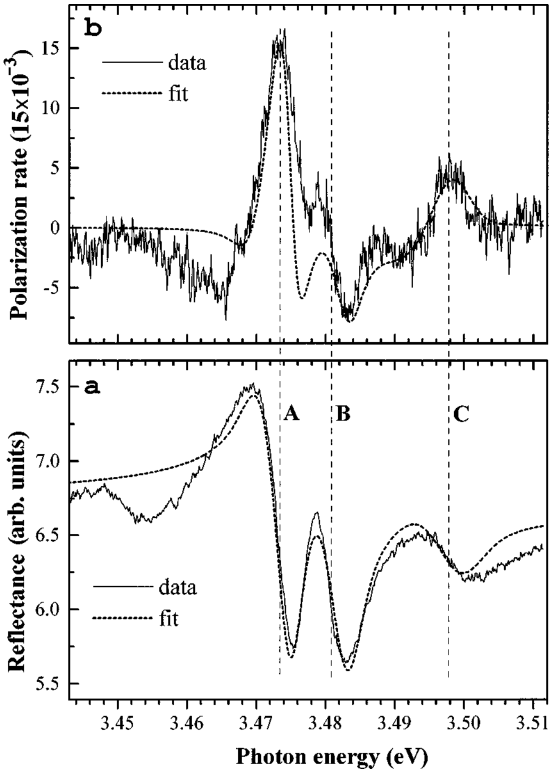

FIG. 1. Reflectance intensity (b) and polarization (a) in GaN at 5.5 T: the fits are plotted with thick dotted curves. The fundamental energies of the three excitons X_A, X_B, and X_C are indicated by vertical dashed lines.

Obtaining the information from the reflectance spectrum requires fitting the line shape using the model described in the previous section, where three oscillators contribute to the dielectric constant. The energies of the excitonic transitions are determined from the fits with a great accuracy. Oscillator strengths α_i and damping factors Γ_i are also calculated. Table I shows the parameters obtained from the fit of the spectrum at 5.5 T. In Fig. 1(b), the dotted line shows the best fit. The fits have been performed with a 60-Å-thick *dead layer* and we have checked that a little variation of this parameter does not significantly affect either quality or numeric results. We have checked that the fit quality is better with a Gaussian line shape than with a Lorentzian one. However, the actual band-gap energy distribution may be somewhat different from this, which may explain the slight misfit be-

TABLE I. Fit parameters at 5.5 T; energies of transition, Zeeman splittings (δE) and effective Landé factors for excitons X_A, X_B, and X_C and Zeeman splittings (ΔE), and effective Landé factors for bands A, B, C.

	X_A	X_B Fit parameters at 5.5 T	X_C
E_0 (eV)	3.4731±0.0002	3.4814±0.0002	3.4977±0.0004
α (meV)	2.94±0.1	2.06±0.1	0.88±0.1
Γ (meV)	3.9±0.3	4.6±0.3	5.9±0.7
δE (meV)	0.25±0.04	−0.03±0.05	0.30±0.08
Exciton	X_A	X_B	X_C
(δE) Splitting (meV/T)	0.055±0.007	−0.007±0.009	0.063±0.015
Effective Landé factor g_{eff}	0.48±0.06	−0.06±0.08	0.54±0.13
Band	A	B	C
(ΔE) Splitting (meV/T)	0.165±0.015	−0.117±0.017	−0.047±0.023
Effective Landé factor g_{eff}	0.95±0.09	−2.0±0.3	−0.8±0.4

tween the experimental and the calculated curves.

In order to analyze the dichroism signal ($\Delta R/R$), the parameters E_{0i}, α_i, and Γ_i have been fixed to the values obtained from the reflectance spectra fits. Only four parameters, δE_i and $P_{BC/A}$, have then been necessary to fit $\Delta R/R$. Table I also presents the results of the fit of $\Delta R/R$. The polarization parameter $P_{BC/A}$ has been found to be equal to 0.028 ± 0.004 at 5.5 T. The dotted line in Fig. 1(a) represents the best fit for $\Delta R/R$.

The parameters presented in Table I allow us to calculate the crystal-field energy and the spin-orbit coupling in direction z and in direction x,y. Their values were found to be $\Delta_1 = 13.1 \pm 0.4$ meV, $\Delta_2 = 6.6 \pm 0.4$ meV, and $\Delta_3 = 5.3 \pm 0.4$ meV, respectively. The eigenvector parameter $a^2 = \alpha_B/\alpha_A$ is calculated to be 0.68. The spin-orbit coupling factors Δ_2 and Δ_3 are relatively close to one another. On the subject of the broadening factors Γ_i, one sees that $\Gamma_A \approx \Gamma_B$, whereas Γ_C is somewhat bigger. One possible explanation of this may be that the energy of the X_C exciton is more sensitive than that of X_A and X_B to a change in the biaxial constraint. Indeed, the biaxial constraint modifies the band energies[3,16] and may not be perfectly homogeneous in our samples. Compared to determinations using only the energies of the three excitons over a set of samples with different biaxial strain,[3] we obtain good agreement on Δ_2 and Δ_3 and a reasonable agreement on Δ_1, of which the exact value depends on the strain of each particular sample. This proves the validity of the model.

Similarly, R and ΔR were analyzed over a range of magnetic fields (between 0 and 5.5 T) from which the energy splittings of the three excitonic transitions as a function of the magnetic field were calculated, as shown in Fig. 2. The error bars are quite large, especially for the X_C exciton. Nevertheless, we believe that estimating the Zeeman splitting for the three excitonic transitions is unique. Given that excitons in a Faraday configuration have an angular momentum $J_z = \pm 1$, the effective Landé factors g_{eff} ($\delta E = g_{\mathrm{eff}} \mu_B B \delta J_z$) for the excitons are calculated. We get the Zeeman splittings and Landé factors shown in Table I.

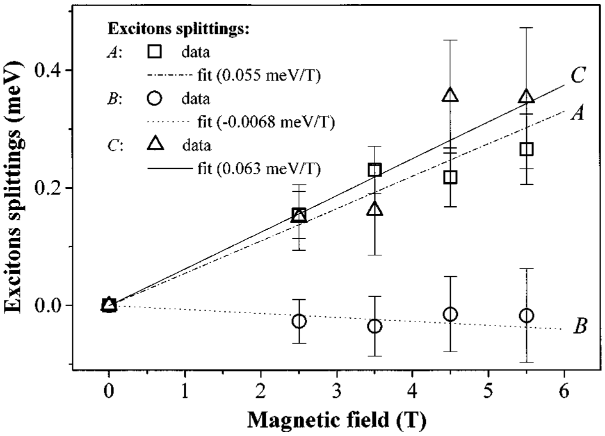

FIG. 2. Energy splittings for the three excitonic transitions δE_i, as calculated using the dichroism method.

The Zeeman splitting for the S band (ΔE_S) has been measured by photoluminescence in a magnetic field perpendicular to the c axis, and reported to be 0.11 ± 0.008 meV/T,[17] that is $g = 1.9 \pm 0.1$. With the reasonable assumption that the S band shows a near isotropic Zeeman splitting; we determined the splittings and g_{eff} values for the valence bands. Our results are shown in Table I. We found a positive Zeeman splitting for the A band, and a negative splitting for the B and C bands, although much more important for the B band. A theoretical model accounting precisely for these results still remains to be established.

The splitting values for the X_A and X_C excitons are very similar, whereas the X_B exciton exhibits an almost zero splitting. This can be explained if we suppose that the splitting of the conduction band S is comparable to the splitting of the B valence band (ΔE_B), and then an accidental cancellation occurs.

J. C. would like to thank the ministerio de Educación y Cultura of Spain for financial support. M. J. would like to thank the Ecole Normale Supérieure in Paris, France for financial support.

---

[1] S. Strite and H. Morkoç, J. Vac. Sci. Technol. B **10**, 1237 (1992).
[2] R. Dingle and M. Ilegems, Solid State Commun. **9**, 175 (1971).
[3] B. Gil, O. Briot, and R. L. Aulombard, Phys. Rev. B **52**, R17 028 (1995).
[4] M. Altarelli and N. O. Lipari, Phys. Rev. B **7**, 3798 (1973).
[5] D. Coquillat, J. P. Lascaray, J. A. Gaj, J. Deportes, and J. K. Furdyna, Phys. Rev. B **39**, 10 088 (1989).
[6] D. Coquillat, F. Hamdani, J. P. Lascaray, O. Briot, and R. L. Aulombard, Phys. Rev. B **47**, 10 489 (1993).
[7] K. Cho, Phys. Rev. B **11**, 1512 (1975).
[8] W. Ekardt, K. Losch, and D. Bimberg, Phys. Rev. B **20**, 3303 (1979).
[9] O. Briot, J. P. Alexis, R. L. Aulombard, and M. Tchounkeu, Mater. Sci. Eng. B **43**, 1–3 (1997).
[10] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).
[11] S. I. Gubarev, Phys. Status Solidi B **134**, 211 (1986).
[12] S. L. Chuang and C. S. Chang, Phys. Rev. B **54**, 2491 (1996).
[13] Y. Chen, B. Gil, H. Mathieu, and J. P. Lascaray, Phys. Rev. B **36**, 1510 (1987).
[14] K. Cho, in *Excitons*, edited by K. Cho, Topics in Current Physics Vol. 14 (Springer-Verlag, Berlin, 1979), pp. 1–54.
[15] H. Shen, S. H. Pan, F. H. Pollak, M. Dutta, and T. R. AuCoin, Phys. Rev. B **36**, 9384 (1987).
[16] B. Gil, F. Hamdani, and H. Morkoç, Phys. Rev. B **54**, 7678 (1996).
[17] D. Volm, T. Streibl, B. K. Meyer, T. Detchprohm, H. Amano, and I. Akasaki, Solid State Commun. **96**, 53 (1995).