Determination of the spin-exchange interaction constant in wurtzite GaN

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Wurtzite GaN grown onto an *A*-plane sapphire exhibits a uniaxial strain because the thermal expansion coefficient of the substrate is anisotropic. Measuring the dependence of the transition energies and of the oscillator strengths on the polarization of light, we deduced the value of the spin-exchange energy in wurtzite GaN: $\gamma \approx 0.6 \pm 0.1$ meV. [S0163-1829(98)52012-7]

I. INTRODUCTION

Group-III nitride semiconductor compounds, such as GaN, appear to be of considerable scientific and commercial importance, especially due to their applications for light-emitting diodes and UV semiconductor lasers.

Optical spectroscopy is a very useful technique for distinguishing the most intimate properties of semiconductors. We used this technique to study the internal structure of the exciton (spin-exchange constant γ, deformation potentials) in GaN.

The application of uniaxial strain to a sample is a way to determine the spin-exchange energy between the hole and the electron in excitons.[1] As it would be difficult to apply a uniaxial strain on an epilayer, we took advantage of the built-in strain in GaN grown perpendicularly to the *c* axis of the sapphire.

The geometry of the sample studied in this work consisted of an epilayer of hexagonal GaN grown onto an *A*-plane sapphire substrate, that is, the (0001) plane of the hexagonal GaN is parallel to the (11$\bar{2}$0) plane of the hexagonal sapphire.[2] In this particular configuration, by decreasing the temperature we can create a controlled anisotropic deformation in the (0001) GaN plane. This is due to the fact that the thermal expansion coefficients of the sapphire substrate are strongly anisotropic ($\alpha_{\|c} = 8.5 \times 10^{-6}$ K^{-1}, $\alpha_{\perp c} = 7.5 \times 10^{-6}$ K^{-1}) and it induces a reduction of the C_{6v} hexagonal symmetry of the GaN lattice to the C_{2v} orthorhombic symmetry. This change of symmetry generates an anisotropy in the optical properties of GaN.

We examined the spectroscopic properties of free excitons and demonstrated that the Γ_5 levels of the GaN grown onto conventional *C*-plane substrates (Al$_2$O$_3$, 6H-SiC, ZnO) are split into the Γ_4 and Γ_2 modes of the orthorhombic symmetry when grown onto *A*-plane substrates. The optical responses of these modes are given by the selection rules and from their splitting we obtained the exciton spin-exchange interaction γ, which was, to the best of our knowledge, unknown until now. We obtained $\gamma \approx 0.6$ meV, and found that the polarization dependence of the oscillator strengths of the excitonic levels, obtained from a line-shape fitting of the reflectance, matched the theory very well.

The paper is organized in the following way: in Sec. II the theoretical problem is briefly described. In Sec. III the experimental results are given and analyzed, γ is calculated, and compared with existing theories, and the results are discussed.

II. THEORETICAL PART

The Hamiltonian of the valence band in wurtzite GaN is well known.[3,4] Taking the *A* band (heavy holes $J_z = \pm 3/2$) as the origin for the energies, one gets (without strain)

$$H_0 = \Delta_1(L_z^2 - 1) + \Delta_2(L_z\sigma_z - 1) + \Delta_3(L_x\sigma_x + L_y\sigma_y),$$

where Δ_1 is the crystal-field parameter due to the wurtzite structure, and Δ_2 and Δ_3 are the spin-orbit coupling constants in the *c* direction and in the perpendicular direction, respectively. In the basis ($|1,1,\uparrow\rangle$, $|1,1,\downarrow\rangle$, $|1,0,\uparrow\rangle$, $|1,-1,\downarrow\rangle$, $|1,-1,\uparrow\rangle$, $|1,0,\downarrow\rangle$), using the notation $|L,L_z,\sigma_z\rangle$, where **L** is the orbital moment, and σ is the spin of the electron, the latter Hamiltonian takes the form

$$H_0 = \begin{pmatrix} H_3 & 0 \\ 0 & H_3 \end{pmatrix} \quad \text{with} \quad H_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -2\Delta_2 & \sqrt{2}\Delta_3 \\ 0 & \sqrt{2}\Delta_3 & -\Delta_1 - \Delta_2 \end{pmatrix}.$$

The effects of the biaxial strain (that is a compression or expansion in the plane perpendicular to *c*, which does not change the wurtzite symmetry), well known in wurtzite GaN,[5] are taken into account through their effects onto the crystal-field parameter Δ_1 and the conduction-band energy E_c. We take $E_c = E_c^0 + \delta_1$ and $\Delta_1 = \Delta_1^0 + \delta_2$, where δ_1 and δ_2 are taken proportional to the value of the biaxial strain, and E_c^0 and Δ_1^0 are the parameters without strain. The uniaxial strain is taken into account in the Hamiltonian H_v for the valence band:

$$H_v = H_0 - \delta_3(|X\rangle\langle X| - |Y\rangle\langle Y|),$$

with δ_3 proportional to the uniaxial strain. When a uniaxial strain exists [i.e., a nonzero $(e_{xx} - e_{yy})$ deformation], the *x* and *y* axes are no longer equivalent. We then preferred a basis containing $|X\rangle$, $|Y\rangle$, and $|Z\rangle$, which transform like the

P_x, P_y, and P_z atomic wave functions at $\mathbf{k}=0$. We have $|1,\pm 1\rangle = (\mp|X\rangle - i|Y\rangle)/\sqrt{2}$ and $|1,0\rangle = |Z\rangle$. In the basis $B = (|X,\uparrow\rangle, |iY,\uparrow\rangle, |Z,\downarrow\rangle, |X,\downarrow\rangle, |-IY,\downarrow\rangle, |-Z,\uparrow\rangle)$, we have

$$H_v = \begin{pmatrix} H_{3v} & 0 \\ 0 & H_{3v} \end{pmatrix} \quad \text{with}$$

$$H_{3v} = \begin{pmatrix} -\Delta_2 - \delta_3 & \Delta_2 & \Delta_3 \\ \Delta_2 & -\Delta_2 + \delta_3 & -\Delta_3 \\ \Delta_3 & -\Delta_3 & -\Delta_1 - \Delta_2 \end{pmatrix}.$$

Coupling an electron in the conduction band to a hole in the valence band, one gets the following Hamiltonian for the fundamental state of the excitons:

$$H_{\text{exc}} = E_c - R^* - H_v + \tfrac{1}{2}\gamma\sigma_h\sigma_e,$$

where E_c is the energy of the conduction band, R^* is the rydberg of the exciton, which will be assumed to be constant, and γ is the spin-exchange interaction constant between the hole and the electron spins. σ_h and σ_e are the Pauli spins matrices of the hole and the electron, respectively. σ_h is then the spin opposite to that of the missing electron in the valence band. We used the spin of the missing electron rather than that of the hole to label the excitonic states.

We used a 12-fold basis, that is, the direct product of the sixfold basis B for the valence band with the twofold basis $(|\uparrow\rangle, |\downarrow\rangle)$ for the conduction band, with the notation $|L, \sigma_{\text{VB},z}, \sigma_{\text{CB},z}\rangle$, where L stands for the wave function of the valence-band orbital (i.e., X, Y, or Z). $\sigma_{\text{VB},Z}$ and $\sigma_{\text{CB},Z}$ are the spin moments of the missing electron in the valence band and of the electron in the conduction band, respectively. The excitonic Hamiltonian can be block diagonalized into two 6×6 matrices:

$$H_{\text{exc}} = \begin{pmatrix} H_{xy} & 0 \\ 0 & H_{Z\varnothing} \end{pmatrix} \quad \text{in the basis } (B_{xy}, B_{z\varnothing}),$$

where $B_{xy} = (|X,\uparrow,\uparrow\rangle, |iY,\uparrow,\uparrow\rangle, |Z,\downarrow,\uparrow\rangle, |X,\downarrow,\downarrow\rangle, |-iY,\downarrow,\downarrow\rangle, |-Z,\uparrow,\downarrow\rangle)$ contains the excitons allowed for dipolar electronic transitions with an electric field perpendicular to c, whereas $B_{z\varnothing} = \{|X,\downarrow,\uparrow\rangle, |-iY,\downarrow,\uparrow\rangle, |-Z,\uparrow,\uparrow\rangle, |X,\uparrow,\downarrow\rangle, |iY\uparrow,\downarrow\rangle, |Z,\downarrow,\downarrow\rangle\}$ contains the excitons allowed for $\mathbf{E}\|c$, as well as the forbidden excitons. We have

$$H_{xy} = H_6 + \frac{\gamma}{2}\begin{pmatrix} -1 & 0 & 0 & 2 & 0 & 0 \\ 0 & -1 & 0 & 0 & -2 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & -1 & 0 & 0 \\ 0 & -2 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix};$$
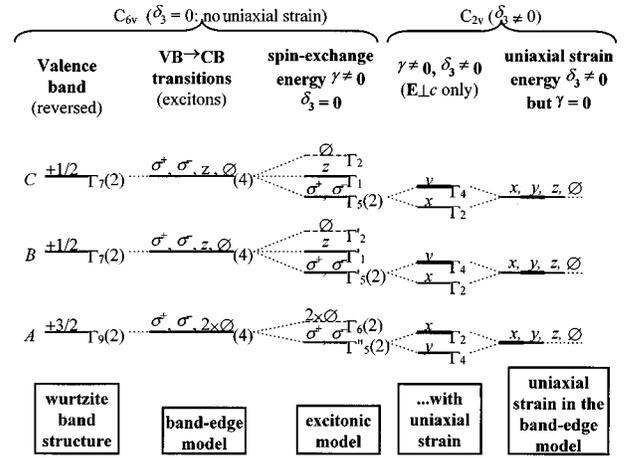

FIG. 1. The excitonic transitions depending on the approximation used for the calculation. "$\varnothing$" stands for forbidden transitions, and x,y,z, for linearly polarized light [when $\delta_3 = 0$, (σ^+, σ^-) are used instead of (x,y)].

$$H_{z\varnothing} = H_6 + \frac{\gamma}{2}\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & -2 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & -2 & 0 & 0 & -1 \end{pmatrix}$$

with $\quad H_6 = E_c - R^* - H_v$.

The exciton states are then the eigenvectors of H_{exc}. Given an exciton state $|\psi\rangle$, its oscillator strength in the X, Y, and Z polarization are, respectively, given by $|\langle X,\uparrow,\uparrow|\psi\rangle + \langle X,\downarrow,\downarrow|\psi\rangle|^2$, $|\langle iY,\uparrow,\uparrow|\psi\rangle - \langle -iY,\downarrow,\downarrow|\psi\rangle|^2$, and $|\langle -Z,\uparrow,\uparrow|\psi\rangle - \langle Z,\downarrow,\downarrow,|\psi\rangle|^2$.

Since our experiments were done in the direction normal to the surface ($\mathbf{k}\|c$), only the X and Y (or σ^+, σ^-) polarizations are available. We can then restrict ourselves to the H_{xy} part of the Hamiltonian.

An overview of the excitonic transitions is given in Fig. 1. In the wurtzite structure (C_{6v} symmetry), the exchange interaction splits some of the excitonic states, but it gives no visible splitting for $\mathbf{k}\|c$ (i.e., $\mathbf{E}\perp c$) because the transitions allowed for $\mathbf{E}\|c$ (labeled as z) cannot be reached. However, the spin exchange modifies the energies and oscillator strength of the allowed transitions[6] (see the excitonic model in Fig. 1, for $\gamma\neq0$ and $\delta_3 = 0$). A uniaxial strain breaking the symmetry between x and y (that is switching to C_{2v} symmetry) causes a change in the oscillator strengths depending on the x or y linear polarization (see Fig. 1: $\delta_3\neq0$ and $\gamma=0$), but to observe an energy splitting requires taking into account the exchange interaction ($\delta_3\neq0$ and $\gamma\neq0$). The reason is that if $\gamma=0$, the Hamiltonian is block diagonal, built from the H_{3v} (3×3) matrix only, leading to only three different energy levels, each one with an oscillator strength depending on the x or y light polarization.

Figure 2 shows the consequences of a nonzero spin-exchange splitting even for usual samples, with a wurtzite symmetry. Indeed, it mixes the A exciton with B and C. This is important because with a negative biaxial strain of the
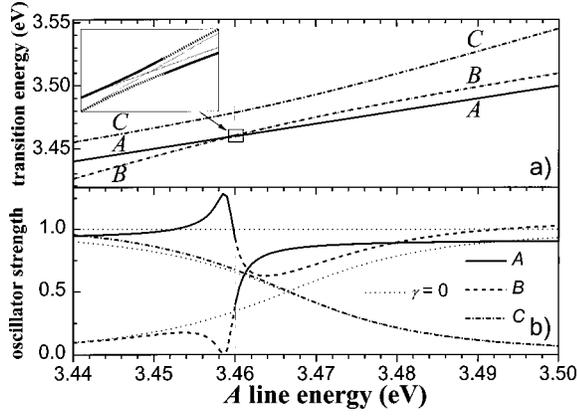
FIG. 2. Calculated transition energies (a) and oscillator strengths (b) in wurtzite GaN depending on the biaxial strain. The crossing between A and B turns to an anticrossing. The thin dotted lines are calculated without a spin-exchange interaction ($\gamma = 0$).

epilayer (which can be achieved in GaN grown onto silicon substrates), a crossing between the A and B lines is known to occur. With the spin-exchange interaction, it turns into an anticrossing [Fig. 2(a)], with a steep variation of the oscillator strengths [Fig. 2(b)], which cannot be measured experimentally for the moment because the energy splitting between the mixed states is much smaller than the transitions linewidth.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 displays the 2 K reflectance spectra of this special sample taken with its c axis ([0001] direction) parallel to the **k** vector of the incident light and with the electric field parallel to the $[1\bar{1}00]$ (hereafter X) direction [Fig. 3(a)] or parallel to the $[11\bar{2}0]$ (hereafter Y) direction [Fig. 3(b)]. Two well-resolved transitions, associated with A,B excitons, can be observed in both spectra. A third broadened structure located at higher energy is attributed to the C exciton, which is degenerated with the continuum of A and B. The first noticeable feature that this spectrum shows is the dramatic oscillator strength variation for A and B excitons as the polarization is changed. Oscillations in the low-energy part of the spectra are due to interference phenomena.

In order to obtain exciton energies and oscillator strengths with great precision we have fitted the reflectivity line shape. We assumed a 60-Å-thick *dead layer*, and modeled the dielectric constant ε using a set of three oscillators, as shown by

$$\varepsilon(k,E) = \varepsilon_b + \sum_{j=1}^{3} \frac{2E_{LTj}E_{0j}}{E_{0j}^2 - [(\hbar^2 k^2)/m_j^*]E_{0j} - E^2 - i\Gamma_j E},$$
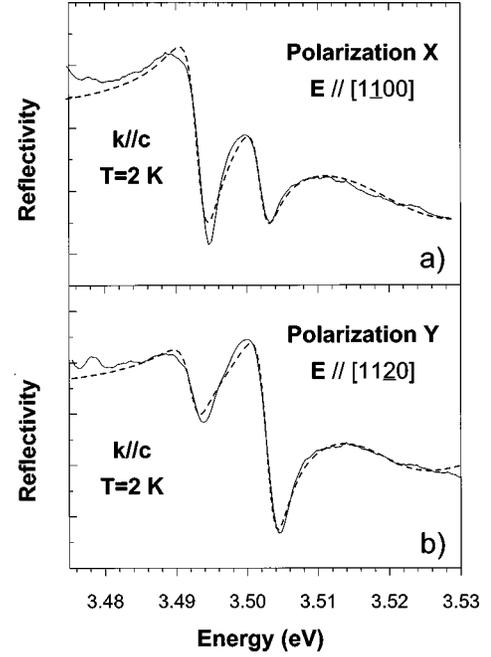

FIG. 3. 2 K reflectance spectra (continuous line) and the corresponding fitting (dashed line) for both X (a) and Y (b) polarizations.

where $\varepsilon_b = 9.5$ (Ref. 7) is the background dielectric constant, E_{0j} is the resonance energy of the j exciton of effective mass m_j^*, Γ_j is the damping factor, and E_{LT} is its oscillator strength. For our purpose the spatial dispersion term ($\hbar^2 k^2/m_j^*$) can be neglected. Dotted lines in Fig. 3 show the best fitting of the data. The parameters obtained from the fitting are listed in Table I. The energy shifts calculated from the fitting of the reflectance structures were $E_A^X - E_A^Y \approx E_B^Y - E_B^X \approx 0.45 \pm 0.05$ meV and the degree of oscillator strength polarization were $\alpha_A^X/\alpha_B^X \approx \alpha_B^Y/\alpha_A^Y \approx 2.4 \pm 0.2$.

As has already been shown,[6] if a value is assumed for the exchange energy γ, the energies of the three excitons A, B, and C for various samples with different biaxial strains allow us to calculate the conduction-band energy $E_c - R^*$ (it is actually the ground level of the excitons, but the rydberg energy R^* cannot be separated from E_c, and is assumed to be constant), the crystal-field parameter Δ_1, and the spin-orbit coupling parameters Δ_2 and Δ_3. The results are comparable to those calculated from a measure of the oscillator strengths.[8]

The origin for biaxial strain is arbitrarily taken for $E_A = 3.470$ eV (energy of the A exciton). Assuming a value for γ, we calculate Δ_1^0, Δ_2, Δ_3, E_c^0, and δ_2/δ_1 (that is, $d\Delta_1/dE_c$). For these parameters, which do not depend on this particular sample, we find $\Delta_1^0 = 8.68$ meV, $\Delta_2 = 5.71$

TABLE I. Fitting parameters for the reflectance.

Polarization	E_A (meV)	$E_{LT,A}$ (meV)	E_B (meV)	$E_{LT,B}$ (meV)	C exciton
X	3.492 35	15.741	3.501.63	6.210	too weak to be
Y	3.491 91	6.314	3.502.11	13.777	fitted correctly
X vs Y	$E_A^X - E_A^Y$	$E_{LT,A}^X/E_{LT,A}^Y$	$E_B^Y - E_B^X$	$E_{LT,B}^Y/E_{LT,B}^X$	
Experimental	0.442	2.493	0.489	2.219	
Calculated	0.47	2.51	0.46	2.20	

TABLE II. Spin-exchange constant γ, averaged cation-anion distance d_{A-B}, and dielectric constant ε for some III-V and II-VI compounds.

	GaN	GaP	GaAs	GaSb	InP	ZnO	ZnS	ZnSe	ZnTe	CdS	CdSe	CdTe
γ (meV)	0.60	0.6	0.25	$\leqslant 0.03$	0.04	5.6	4.0	1.0	0.21	2.5	0.4	0.045
d_{A-B} (Å)	2.340	2.360	2.448	2.639	2.535	2.306	2.342	2.454	2.641	3.025	3.061	2.806
ε	9.5	10.8	12.4	15.7	12.35	8.1	8.5	8.6	9.67	8.67	9.58	10.2
Struct.	W	ZB	ZB	ZB	ZB	W	ZB	ZB	ZB	W	W	ZB
Ref.	10	11,12	13,14	15,16	17	1,18	1	1	9	1,18	1,18	9

meV, $\Delta_3 = 5.88$ meV, $E_c^0 = 3.4703$ eV, $\delta_2/\delta_1 = 0.956$. For these particular experiments, we also found $\delta_1 = 22.78$ meV and $\delta_2 = 21.78$ meV (that is, $E_c = 3.4931$ eV and $\Delta_1 = 30.46$ meV, which corresponds to a very strong biaxial compression in comparison to the usual samples).

On the A-plane sapphire, the reflectance exhibits in one linear polarization a strong structure corresponding to the A exciton, and a weaker one for the B exciton, whereas the contrary is observed in the perpendicular polarization. The amount of polarization allows us to determine the δ_3 parameter, corresponding to the uniaxial strain. Here, we calculated $\delta_3 = -2.05 \pm 0.2$ meV.

If a nonzero δ_3 parameter exists, an energy shift of the transitions (especially A and B) is calculated when the polarization is changed from one to the other, as soon as the spin-exchange interaction is taken into account. This is then a way to calculate the spin-exchange energy γ, which can be adjusted so as to be consistent with the value assumed at the beginning of the procedure. The method rapidly converges to the final value $\gamma = 0.597 \pm 0.100$ meV.

Our determination of γ for GaN is in reasonable agreement with the values obtained from static stress measurements, for GaP, GaAs, and GaSb (see Table II). Moreover, these values (including GaN) show an exponential dependence on the interatomic distance.[9] This can be explained assuming that γ can be approximated by an exchange integral of the atomic functions of cations and anions. If we compare with the values found for other series, in II-VI semiconductors, we can observe that γ shows a systematic increase when going from the III-V to the Zn-VI and Cd-VI compounds. The decreasing ionicity and the increasing dielectric constant ε may also contribute to the decrease of the spin-exchange energy γ when going to heavier anions, that is, when going, for example, from GaN to GaP, GaAs, and GaSb.

Using a theoretical model created for II-VI compounds,[18] γ has been estimated to be near 2 meV.[6] The discrepancy with our experimental value may be due to a lower validity of this model for III-V compounds. Besides, our value for γ correctly matches the splitting obtained in Ref. 19 in photoluminescence depending on the polarization.

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