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Exciton Energy Structure in Wurtzite GaN

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Results of theoretical and experimental magneto-optical studies of free excitons in wurtzite GaN are presented. The direct photoluminescence from free exciton states of high-quality GaN epilayers was studied by polarization-dependent magneto-optical measurements in magnetic fields up to 15 T. Zeeman splittings and diamagnetic shifts of the $n = 1$ and $n = 2$ states of the A exciton were observed for magnetic fields parallel and perpendicular to the hexagonal axis. The experimental data are described by a theory of the exciton energy structure in hexagonal semiconductors with wurtzite symmetry in the framework of the quasi-cubic approximation.

1. Introduction

The investigation of free excitons in semiconductors is important for understanding the electronic structure and optical properties of these materials. Exciton energy levels depend strongly on band structure, the values of electron and hole effective masses, the symmetry of the crystal field, and the presence of an external field, e.g., a magnetic field or strain [1]. Magneto–optical experiments are an important tool to obtain basic semiconductor parameters, such as electronic g-factors and carrier effective masses [2], [3]. The electronic structure and optical properties of the group-III nitrides GaN, InN and AlN and their ternary alloys are up to now only rarely understood. For GaN, data of the effective masses, g-values, and exciton energy level splittings are still incomplete and exhibit a considerable scatter [4 to 9]. In this paper we describe theoretically magneto-optical properties of wurtzite GaN and obtain several of these parameters from comparison with experimental data.

2. Experimental Results

For these studies, high-quality GaN epilayers of 300 μm (sample I) and 400 μm thickness (sample II) were grown on (0001) sapphire by hydride vapor-phase epitaxy (HVPE). Additional studies were performed using epitaxial lateral overgrown GaN layers (sample III) grown on (0001) sapphire by HVPE and metalorganic vapor phase

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epitaxy. Details of the growth procedure are given in [10]. Photoluminescence (PL) measurements at 2 K were performed under continuous wave (cw) excitation at 325 nm using a HeCd laser for samples I and II, and at 351 nm using an Ar laser for sample III. We used a 15 T split-coil magnet for the magnetoluminescence experiments and an immersion cryostat for zero-field experiments. In order to obtain the spectral peak positions with high accuracy, line shapes were fitted to the measured spectra using Gaussian and Voigt line shapes.

Although the low-temperature PL of undoped GaN layers is typically dominated by strong emission from donor bound excitons [7, 11, 18], the $n = 1$ ground states of the A, B, and C excitons are clearly identified in the free exciton emission for samples I and II. Fig. 1 shows the PL spectra for sample II. For sample III the ground state emission of the B and C exciton is less intensive and depends also on the site of the sample. Additionally, fine structures of four lines are observed around the $n = 2$ excited state of the A exciton in all three samples (see Fig. 1). We assign two of the lines, marked 1 and 2, to the emission from an excited exciton bound to a ground state of a donor (in agreement with [11]); and the lines labeled 3 and 4 to the emission from the $n = 2$ excited states of a free A exciton. The splitting between the A, B, and C-exciton ground states, Δ_{AB} and Δ_{AC}, are determined to (5.5 ± 0.1) meV and (22.0 ± 0.1) meV for sample I.

The fine structure of the A exciton ground state has been studied for different propagation directions and polarizations of the emitted light. Emission from two transverse exciton–polariton branches Γ_{5T1} and Γ_{5T2} has been observed in zero magnetic field in the surface (wave vector $\mathbf{k} \parallel \mathbf{c}$) geometry, where $\mathbf{c}$ is the hexagonal symmetry axis. In the parallel polarized ($\mathbf{E} \parallel \mathbf{c}$) PL in the edge ($\mathbf{k} \perp \mathbf{c}$) geometry we have identified emission from the longitudinal Γ_{5L} state and the forbidden Γ_6 state. This allows us to deter-

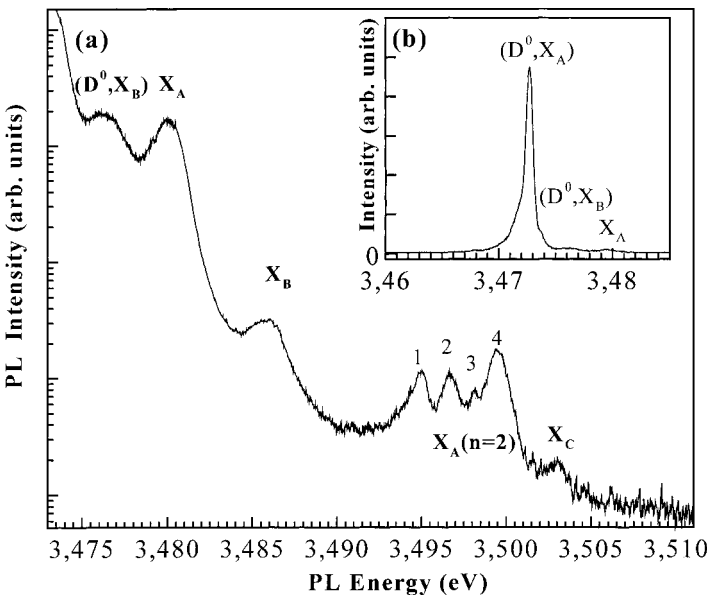

Fig. 1. Direct photoluminescence from excitonic states in GaN on a a) logarithmic b) linear intensity scale. (D^0, X) denotes a donor bound exciton. Details are discussed in the text

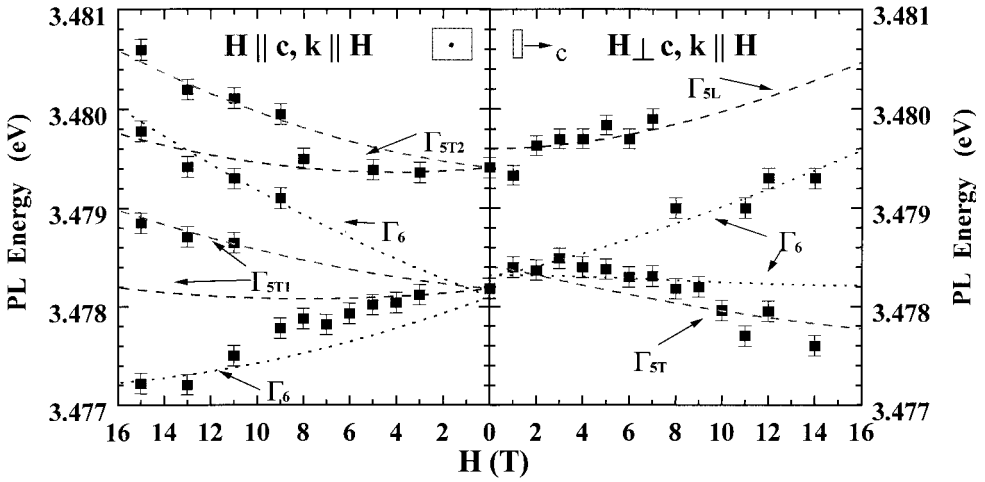

Fig. 2. Dependence of the energy levels of the $n = 1$ state of the A exciton on magnetic field for $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \perp \mathbf{c}$ in Faraday configuration (σ polarization)

mine the values of the electron–hole spin exchange splitting $\Delta_{\text{exc}} = 0.12 \pm 0.1$ meV and of the longitudinal–transverse splitting $\Delta_{\text{LT}} = 1.0 \pm 0.2$ meV. The Zeeman splittings and diamagnetic shifts of the $n = 1$ and $n = 2$ states of the A exciton have been observed for parallel and perpendicular directions of the magnetic field in Faraday geometry. The dependence of the energy levels of the $n = 1$ state of the A exciton on the magnetic field is shown for sample I in Fig. 2 (the small variation of the zero field exciton transition energies in different geometries is caused by slight variations of the residual stain on different sides of the sample). This magnetic field dependence is described (see the dashed curves) by simple expressions which contain the fine structure splittings Δ_{exc} and Δ_{LT}, Zeeman terms, and diamagnetic shifts. For $\mathbf{H} \parallel \mathbf{c}$, both the twofold degenerate transverse polariton states $\Gamma_{5\text{T1}}$ and $\Gamma_{5\text{T2}}$ exhibit a Zeeman splitting with an effective g-factor given by the difference of the electron and hole effective g-factors $|g_{\text{e}}^{\parallel} - g_{\text{hA1}}^{\parallel}|$. The g-factor for the Γ_6 state is given by the sum $|g_{\text{e}}^{\parallel} + g_{\text{hA1}}^{\parallel}|$ (the observation of this forbidden transition at the large magnetic fields can be explained by a small deviation of the wave vector from the parallel direction). For $\mathbf{H} \perp \mathbf{c}$ a linear Zeeman effect between the Γ_5 and Γ_6 states is given in terms of the electron effective g-factor $g_{\text{e}}^{\perp}$. We obtained the electron and hole effective g-factors: $g_{\text{e}}^{\parallel} = 1.95 \pm 0.05$, $g_{\text{e}}^{\perp} = 2.0 \pm 0.05$, and $g_{\text{hA1}}^{\parallel} = 1.1 \pm 0.05$ and values of exciton diamagnetic shifts: $D_{\text{A1}}^{\parallel} = (2.3 \pm 0.2)$ μeV/T^2 and $D_{\text{A1}}^{\perp} = (1.3 \pm 0.2)$ μeV/T^2.

3. Theoretical Consideration

The Hamiltonian of the relative electron–hole motion in a magnetic field in a hexagonal semiconductor is:

$$\hat{H}_{\text{exc}}(\mathbf{k}) = \hat{H}_{\text{e}}\left(\mathbf{k} + \frac{e}{\hbar c}\mathbf{A}\right) - \hat{H}_{\text{h}}\left(-\mathbf{k} + \frac{e}{\hbar c}\mathbf{A}\right) - \frac{e^2}{\sqrt{\varepsilon_0^{\parallel}\,\varepsilon_0^{\perp}\,(x^2 + y^2) + \varepsilon_0^{\perp 2}\,z^2}} + \hat{V}(\mathbf{r})\,, \qquad (1)$$

where $\mathbf{k}$ is the wave vector of the relative motion, $(x, y, z) = (\mathbf{r})$ are the relative electron–hole coordinates, e is the free electron charge, $\mathbf{A} = (1/2)\,[\mathbf{H} \times \hat{\mathbf{r}}]$ is the vector potential of the magnetic field, and $\varepsilon_0^{\parallel}$ and $\varepsilon_0^{\perp}$ are the static dielectric constants for electric fields parallel and perpendicular to the c-axis (which is assumed to coincide with the z direction). The last term in Eq. (1) describes the corrections to the electron–hole Coulomb interaction connected with the differences between the static and high frequency dielectric constants. We chose it in such form that, after the substitution of the new coordinate $z' = z\sqrt{\varepsilon_0^{\perp}/\varepsilon_0^{\parallel}}$, the complete isotropic interaction potential $-e^2/\varepsilon_0 r' + \hat{V}(r')$ is the Haken potential [12] with the averaged static ($\varepsilon_0 = \sqrt{\varepsilon_0^{\parallel}\varepsilon_0^{\perp}}$) and high frequency ($\varepsilon_\infty = \sqrt{\varepsilon_\infty^{\parallel}\varepsilon_\infty^{\perp}}$) dielectric constants. The electron Hamiltonian $\hat{H}_{\mathrm{e}}$ has the form:

$$\hat{H}_{\mathrm{e}}(\mathbf{k}) = \frac{\hbar^2}{2m_{\mathrm{e}}^{\parallel}}\, k_z^2 + \frac{\hbar^2}{2m_{\mathrm{e}}^{\perp}}\,(k_x^2 + k_y^2) + g_{\mathrm{e}}^{\parallel}\mu_{\mathrm{B}}(S_{\mathrm{e}z}\, H_z) + g_{\mathrm{e}}^{\perp}\mu_{\mathrm{B}}(S_{\mathrm{e}x}H_x + S_{\mathrm{e}y}H_y)\,, \qquad (2)$$

where $m_{\mathrm{e}}^{\parallel}$ and $m_{\mathrm{e}}^{\perp}$ are the parallel and perpendicular effective electron masses, $\mu_{\mathrm{B}} = \hbar/2m_0c$ is the Bohr magneton, m_0 is the mass of free electron, and S_{e} is the electron spin 1/2 Pauli matrix. We write the effective Hamiltonian for the hole $\hat{H}_{\mathrm{h}}$ in the framework of the quasi-cubic approximation [13] taking, in addition, the anisotropy of the spin–orbit interaction into account:

$$-\hat{H}_{\mathrm{h}}(\mathbf{k}) = \frac{\hbar^2}{2m_0}\,[(\gamma_1 + 4\gamma)\,k^2 - 6\gamma(\mathbf{k}\cdot\hat{\mathbf{I}})^2] - \frac{2}{3}\,\Delta_{\mathrm{so}}^{\parallel}\left[(\hat{I}_z\hat{S}_{\mathrm{h}z}) - \frac{1}{2}\right] - \frac{2}{3}\,\Delta_{\mathrm{so}}^{\perp}(\hat{I}_{\perp}\hat{S}_{\mathrm{h}\perp})$$
$$-\Delta_{\mathrm{cr}}\,[\hat{I}_z^2 - 1] - \mu_{\mathrm{B}}(1 + 3\gamma + 3\kappa)\,(\hat{\mathbf{I}}\cdot\mathbf{H}) + \mu_{\mathrm{B}}g_0(\mathbf{S}_{\mathrm{h}}\cdot\mathbf{H})\,. \qquad (3)$$

Here, γ_1 and $\gamma = \gamma_2 = \gamma_3$ are the Luttinger parameters [14], κ is the magnetic Luttinger parameter [14], $S_{\mathrm{h}} = 1/2$ is the hole spin, $I = 1$ is the spin 1 matrix of the hole, g_0 is the free electron g–factor, Δ_{cr} is the crystal field splitting, and $\Delta_{\mathrm{so}}^{\parallel}$ and $\Delta_{\mathrm{so}}^{\perp}$ are the spin–orbit coupling parameters. At zero magnetic field the Hamiltonian Eq. (3) describes the three valence subbands A, B, and C with the respective splittings given by [13]:

$$\Delta_{1,2} = \frac{1}{2}\left[\Delta_{\mathrm{so}}^{\parallel} + \Delta_{\mathrm{cr}} \mp \sqrt{\left(\Delta_{\mathrm{cr}} - \frac{\Delta_{\mathrm{so}}^{\parallel}}{3}\right)^2 + \frac{8}{9}\,\Delta_{\mathrm{so}}^{\perp 2}}\right]. \qquad (4)$$

The effect of the external biaxial strain can be taken into account within the model by modifying the values of the crystal field and the band gap energies [6].

With the Hamiltonians Eqs. (1) to (3) we have investigated the A, B, and C exciton states of symmetry 1S , 2S, and 2P, using the perturbation method developed in Refs. [15, 16] for cubic semiconductors. The exciton binding energies, the values of hole effective g-factors and exciton diamagnetic shifts are expressed analytically in terms of the parameters of our Hamiltonians in second order perturbation theory. In contrast to the approaches of Refs. [2, 3], our theory takes into account the interaction between all the exciton states belonging to the A, B, and C valence subbands. This is essential for GaN because of the relatively small splittings between them. The ground state energies of the A and B excitons in zero magnetic field were previuosly obtained in [17] by a similar approach in the framework of the two valence subbands model.

We have fitted the effective masses and energy parameters of the Hamiltonians Eqs. (1) to (3) in order to describe the experimental values, given in the previous section (the distance between 1S and 2S A exciton state was taken as (18.5 ± 0.3) meV). Two different sets of dielectric constants have been used for calculations: (a) $\varepsilon_0^{\parallel} = 10.1$, $\varepsilon_0^{\perp} = 9.28$, $\varepsilon_\infty^{\parallel} = \varepsilon_\infty^{\perp} = 5.29$ [18] and (b) $\varepsilon_0^{\parallel} = 10.4$, $\varepsilon_0^{\perp} = 9.5$, $\varepsilon_\infty^{\parallel} = \varepsilon_\infty^{\perp} = 5.35$ [19]. The best description was found for the electron effective masses $m_e^{\parallel} = 0.22 m_0$, $m_e^{\perp} = (0.21 \pm 0.01)\, m_0$ for both sets. The effective masses of the hole of the A valence subband (they are related to the Luttinger parameters by $m_A^{\parallel} = m_0/(\gamma_1 - 2\gamma)$ and $m_A^{\perp} = m_0/(\gamma_1 + \gamma)$ [13]) and magnetic Luttinger parameter are: $m_A^{\parallel} = (0.85 \pm 0.1)\, m_0$, $m_A^{\perp} = (0.16 \pm 0.01)\, m_0$, and $\kappa = 0.75 \pm 0.15$ for the set (a) and $m_A^{\parallel} = (1.1 \pm 0.1)\, m_0$, $m_A^{\perp} = (0.17 \pm 0.01)\, m_0$, and $\kappa = 0.75 \pm 0.15$ for the set (b). The energy splitting parameters are: $\Delta_{cr} = (12.3 \pm 0.1)$ meV, $\Delta_{so}^{\parallel} = (18.5 \pm 0.2)$ meV and $\Delta_{so}^{\perp} = (18.0 \pm 0.2)$ meV. The same calculations without the Haken potential correction lead to larger values of the hole effective masses with $m_A^{\parallel} \geq 4.0 m_0$. Thus, including the Haken corrections is important for the realistic determination of the effective mass parameters. These corrections in zero magnetic field are in the order of 25 to 30 % for the 1S state and 12% for the 2S state (a more exact account of these corrections, also with a magnetic field, is needed). The energy structure of the $n = 2$ states of the A exciton in zero field depends strongly on the effective mass parameters. The Haken correction, however, does not effect states with P symmetry and makes the 2S states the lowest ones.

4. Conclusion

We have developed a new theory for the exciton energy structure in hexagonal semiconductors and applied it to describe the experimental magneto-optical data on free exciton emission in wurtzite GaN. A more detailed analysis of the experimental magneto-optical data on the ground and excited states of A and B excitons, which will allow us to determine all important basic parameters of GaN, is in progress.

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