ELSEVIER

Journal of Crystal Growth 189/190 (1998) 639–643

JOURNAL OF CRYSTAL GROWTH

The exciton–polariton effect on the fluorescence properties of GaN on sapphire

Bernard Gil[a,*], Axel Hoffmann[b], Sandra Clur[a], Ludger Eckey[b], Olivier Briot[a], Roger-Louis Aulombard[a]

[a] *Centre National de la Recherche Scientifique, Groupe d'Etude des Semiconducteurs, Université de Montpellier II, Case Courrier 074, 34095 Montpellier Cedex 5, France*

[b] *Institut fürFestkörperphysik, Technische Universität Berlin, Hardenbergstrasse. 36, 10623 Berlin, Germany*

Abstract

We study the free exciton fine structure and the contribution of propagating excitations in the lower-polariton and upper-polariton branches (LPB and UPB) in the 2 K fluorescence spectrum of GaN on Al_2O_3. The latter effect is observed for both *A* and *B* lines. A line-shape fitting of the photoluminescence was made using four Lorentzian functions. The distribution of polaritons in the UPB(*A*), LPB(*B*) and UPB(*B*) are found consistent with a Boltzmann electronic temperature of 29 K when exciting the fluorescence with a He–Cd laser at 325 nm. The longitudinal–transverse splittings can be extracted from the splittings between energies of dips in the PL bands at 3489.4 and 3497.8 meV and the values of the transverse excitons are smaller than 2 meV.

1. Introduction

The free exciton, the first excited state of the crystal with $N-1$ electrons in the valence band and one electron in the conduction band cannot be simply considered as an electron–hole pair in Coulombic interaction. It is an elementary excitation of the crystal which propagates with a given wavelength. Its formation energy is slightly lower than the fundamental band gap, and in addition to its genuine internal structure due to the interaction of the spins of the conduction electron and of the valence hole, it may exhibit an internal structure due to eventual band degeneracies. Interpretation of the optical properties a semiconductor requires the development of sophisticated models where both the exciton fine structure and the electron–photon interaction are treated on the same footing. Determination of these parameters is far from easy in GaN: all samples are obtained under various strain conditions, a situation which causes each epilayer to have particular properties, by observing spectroscopic details very closely [1]. In the next section, we give in detail the internal structure of the free excitons in wurtzite GaN and present its evolution with strain. Experimental results are

* Corresponding author. Tel.: +33 467 143 924; fax: +33 467 143 760; e-mail: gil@ges.univ-montp2.fr.

0022-0248/98/$19.00
PII S0022-0248(98)00227-9

shown which reveal a possibility to observe in photoluminescence the forbidden exciton levels as in CdS [2]. This experiment is performed on a thick (300 μm sample grown by hydride vapour phase epitaxy). Then we address the longitudinal–transverse splitting issue in a thinner sample (2 μm) deposited by metal organic vapour phase epitaxy on *C*-plane sapphire.

2. Exciton fine structure at zone centre

The twelvefold exciton transforms according to $3\Gamma_5 + 2\Gamma_1 + 2\Gamma_2 + \Gamma_6$. The construction of such exciton states from Γ_7^c, Γ_9^v, Γ_7^v states (we add upperscripts to avoid confusion) can be found in Ref. [3]. The two-fold Γ_6 exciton is forbidden, as also are the two Γ_2 ones. The three Γ_5 excitons are created using an adapted photon, σ-polarized (electric field $\perp[0\,0\,0\,1]$) and the two Γ_1 excitons are created for π-polarized photons (electric field $//[0\,0\,0\,1]$). Following Ref. [3], the exciton Hamiltonian Ξ_{exc} is written as

$$\Xi_{exc} = H_{c=0} + H_{cstrain} + H_{v=0} + H_{vstrain} + H_{exc},$$

where $H_{v=0}$ ($H_{c=0}$) is the strain-free valence (conduction) band Hamiltonian and $H_{vstrain}$ ($H_{cstrain}$) is corresponding Hamiltonian, which accounts for the strain-related effects on the evolution of extreme bands. The last operator can be written as

$$H_{exc} = R^* + 1/2\gamma\sigma_h \cdot \sigma_c,$$

where R^* is the exciton binding energy and the last term is the crystalline exchange interaction. Operators σ_h and σ_c operate on valence hole and conduction electron spin functions. Fig. 1 illustrates theoretical calculation of the strain dependence of these exciton levels in epilayer grown (0 0 0 1) substrates, with pure biaxial stress. γ was taken to be 2 meV [3].

We note that the Γ_5–Γ_6 splitting is predicted to be very small as shown on Fig. 2. To have some chance of observation of the Γ_6 forbidden line in photoluminescence, like it was done for CdS [2], requires the presence of very narrow lines. Results obtained in Ref. [4], and shown on Fig. 3 demonstrate the possibility of observing this Γ_6 mode in photoluminescence. A striking difference is

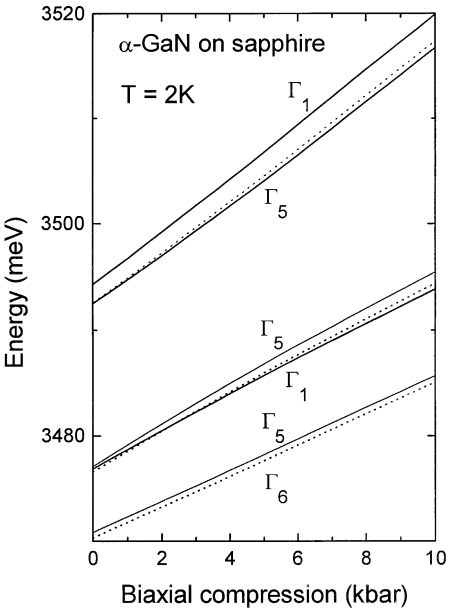

Fig. 1. Fine structure splitting of the excitons in GaN and their evolution with biaxial strain. Dotted lines correspond to forbidden Γ_2 and Γ_6 excitons.

observed between the perpendicular and parallel polarizations in the low-energy peak positions in Fig. 3a and Fig. 3b, respectively. In the perpendicular polarization this peak is found at 3.47904 eV while in parallel polarization 3.47892 eV is measured. On the basis of group theoretical argumentation we identify the latter value with the energy of the spin triplet state of the *A*-exciton. Thus, the energy difference of 120 ± 100 μeV between the peaks noted Γ_6 and Γ_{5L} is ascribed to the splitting of these states caused by the exchange interaction. It is found slightly smaller than it was theoretically predicted in Ref. [3]. The upper value (220 μeV) is consistent with $\gamma = 0.6$ meV [5].

3. Longitudinal transverse splittings

Due to the *k*-selection rule for optical matrix element, excitons having exactly the photon *k* vector should radiate. In the pure bulk material, and in the simplest model the coupling of the electromagnetic field represented by a photon having an energy $E = hkc/2\pi$ with the exciton $E = E_T +$

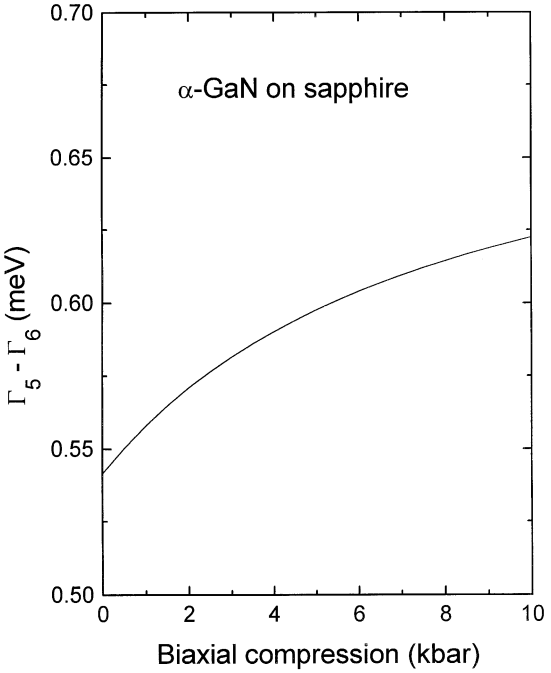

Fig. 2. Strain-induced evolution of the Γ_5–Γ_6 splitting in GaN, according to the calculation of Ref. [3].

$h^2k^2/8\pi^2$m creates the exciton–polariton picture [6]. This coupling relaxes the k selection rule and transforms the fluorescence mechanism into a transport of the coupled excitation from the depth it is created, towards the surface, where a part of it is reflected, and the remainder is transmitted. Under non-resonant excitation conditions, an electron–hole pair created in the continuum of states will relax towards lower energies within the two polariton branches. In particular, it will thermalize efficiently via, most probably, acoustic phonon emission within the low polariton band, down to the knee of the polariton dispersion, just below the transverse frequency, due to the high density of states in this region. Below the transverse frequency, when the wave function becomes more and more photon-like, the decrease of both the scattering matrix element and of the density of final states; combined with the large increase of the group velocity $d\omega/dk$ causes the radiative lifetime to dominate over the thermal relaxation (in this region, the escape of the photon out of the crystal

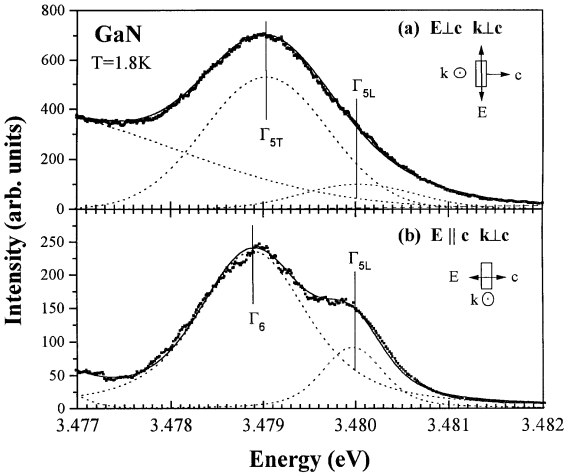

Fig. 3. The emission from the $n = 1$ state of the A-exciton in a free-standing 300 mm GaN epilayer in perpendicular (a) and parallel (b) polarizations allows to determine the LT splitting and the energy of the "forbidden" triplet exciton.

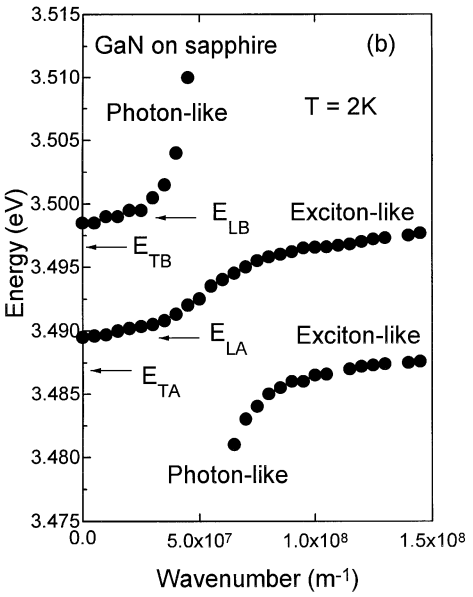

Fig. 4. Dispersion relations for the exciton polariton in a thin GaN epilayer grown on C-plane sapphire. The figure is taken from Ref. [7].

becomes very efficient). This gives a "polariton relaxation bottleneck" and, at the end, the polariton exhibits a pronounced distribution peak just below the exciton energy. Under resonant excitation

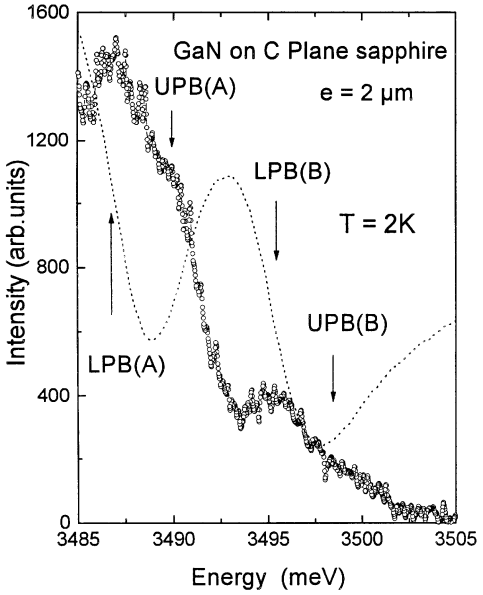

Fig. 5. The 2 K reflectance spectrum (dashed line) and the corresponding 2 K photoluminescence (open circles) spectrum which shows the LPB and UPB contributions to the GaN fluorescence. The excitation energy is the 325 nm radiation of the He–Cd laser. The excitation density is 1 W cm^{-2}.

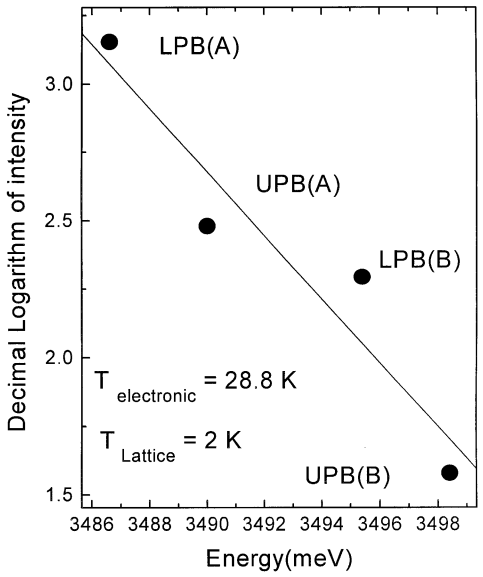

Fig. 6. The spectral distribution of polaritons in the GaN epilayer.

conditions, a "cold", spatially nonuniform polariton distribution would be created at the semiconductor surface. This would produce a strong enhancement of the radiative efficiency and would lead to the formation of a single luminescence peak with no reabsorption dip at ω_L [7]. The situation is much more complicated in GaN since we have two oscillators A and B which interact as shown in Fig. 4, and we expect four photoluminescence peaks [8]. They are effectively found, when exciting at 325 nm, using the radiation of the He–Cd laser, as shown in Fig. 5.

A line-shape fitting was made using four Lorentzian functions. To fit the data, they have to be centred at 3486.6, 3490, 3495.4 and 3498.4 meV, respectively. We note that this sample experiences a strong biaxial compression [1]. The widths of these Lorentzians are 6.87, 2.65, 2.16 and 2.23 meV, respectively. The heights used to fit the PL spectrum of Fig. 1 are 1425, 303, 198 and 38 in arbitrary units. These peaks correspond to photoluminescence maxima at 3486.6 and 3495.4 meV and are labelled LPB(A) and LPB(B) in Fig. 5. There is also a significant population of the upper-polariton branch which gives the high-energy contribution peaks labelled UPB(A) and UPB(B) in the figure.

The logarithmic plot of the intensities of these four peaks shown in Fig. 6. Assuming a Boltzmann distribution for the carriers, we find an electronic temperature about 29 K. Finally, we emphasise the fact that the LT splittings for B and C excitons, which are roughly proportional to the exciton oscillator strength [9], exhibit strong strain dependence as shown on Fig. 7 and are smaller than 2.4 meV and 1.7 meV in this sample. The larger experimental values result of thermalization effect in the polariton branches [2].

4. Conclusions

The observation of LT splittings and exciton fine structure in GaN have been reported. The observation of exciton spin triplet states was made on samples grown by HVPE. In case of a 2 μm thin sample deposited by MOVPE we could observe photoluminescence due to LPB and UPB branches of the A and B polaritons. This observation is

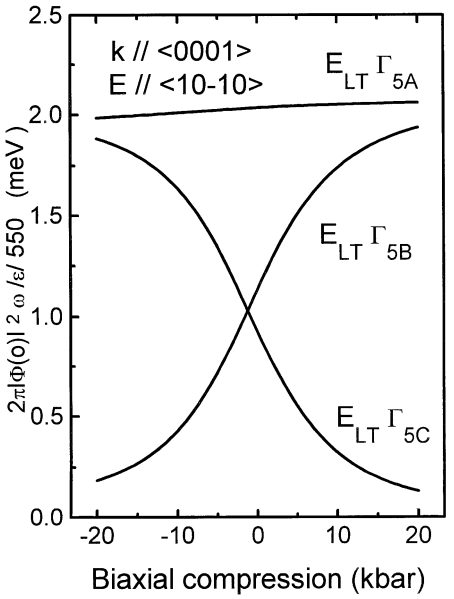

Fig. 7. Evolution of the LT splittings as a function of the biaxial compression in GaN.

favored by the strong biaxial compression state of this epilayer. The LT splitting is found to be different in the epilayers and in the HVPE sample, as also the oscillator strengths and the broadening parameters used for the line-shape fitting. In thin layers the polariton experiences regions of fluctuating residual strain. This changes the self-energies of the oscillators and has subsequent impact on the broadening parameters which are significantly larger in epilayers than in samples grown by HVPE. The net result is that we need higher oscillator strengths to match the results of the reflectance experiment to that of the calculation. It is also important to stress out that the dispersion relation are extremely different depending on whether or not the broadening parameters are included. If we assume that most of their experimental value results from polariton sampling of differently strained regions, it is obvious that the physical meaning of the large experimental values of the gammas is poor if it is to plot the dispersion of the polaritons.

Acknowledgements

This work was partly supported by the French–German joint research programme "PROCOPE" number 98134.

References

[1] B. Gil, O. Briot, R.L. Aulombard, Phys. Rev. B 52 (1995) R17028.
[2] C. Benoit à la Guillaume, A. Bonnot, J.M. Debever, Phys. Rev. Lett. 24 (1970) 1235.
[3] B. Gil, O. Briot, Phys. Rev. B 54 (1997) 2530.
[4] A. Hoffmann, L. Eckey, Proc ICSC-IIINs, Stockholm, 1997, Trans Tech. Publications, 1998, p. 1259.
[5] M. Julier, J. Campo, B. Gil, J. Lascaray, S. Nakamura, Phys. Rev. B 57 (1998) R6791.
[6] J.J. Hopfield, Phys. Rev. 112 (1958) 1555.
[7] C. Weisbuch, R. Ulbrich, J. Lumin. 18/19 (1979) 27.
[8] B. Gil, S. Clur, O. Briot, Solid State Commun. 104 (1997) 267.
[9] B. Gil, Gallium Nitride, in: J.I. Pankove, T.D. Moutsakas, (Eds.), Semiconductors and Semimetals, Academic Press, New York, in press.