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Excitonic Fine Structure and High Density Effects in GaN

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Abstract

The excitonic fine structure of GaN is investigated by means of polarized photoluminescence measurements and magnetooptical experiments. From a careful analysis of the data the level splittings of the n=1 state of the A-exciton in GaN and the electron and hole g-values are obtained. Photoluminescence and optical-gain measurements at intermediate and high excitation levels reveal that excitonic processes as well as the recombination of the electron-hole plasma contribute to the gain in thin epitaxial layers.

Introduction

Despite the recent development of the first multilayer nitride laser structure [1] a thorough understanding has neither been achieved of the basic optical and electronic properties of the nitrides, nor of the physical processes causing stimulated emission. Localized biexcitons [2], the electron-hole plasma [3] and band-to-band recombination [4] have been claimed responsible for the laser mechanism in group-III-nitride heterostructures Most investigations have been limited to room temperature not allowing an unambiguous identification of the electronic processes involved. With increasing temperature the contribution of phonon-assisted processes becomes larger resulting typically in a broad spectral region of optical amplification. In our previous work [5] we studied the gain spectra of thick quasi-bulk GaN between 2 K and room temperature and found that excitonic processes add to the gain at high temperatures. In the present paper our studies of the optical gain in thin GaN epilayers at high excitation levels are presented. For the identification of the mechanisms providing optical amplification in GaN useful information is obtained from high-density effects on the spontaneous and stimulated photoluminescence (PL).

In the field of the basic optical and electronic properties the investigation of excitons plays a key role. There has been a lot of progress in this field in recent years, but the excitonic fine structure is still subject to fundamental research and discussions. For many wide-gap semiconductors it was investigated by means of transmission and reflection spectroscopies. For the case of GaN reflection spectra have been published by many groups revealing mainly the energy differences between the three top valence bands and some fine structure due to higher excited states[e.g., 6]. Transmission spectroscopy in the excitonic range, however, could not reveal any fine structure, mostly because only light polarized perpendicular to the c-axis can be used for epitaxial layers. Much of the fine structure information on excitons in hexagonal wide-gap semiconductors was obtained from the 'forbidden' polarization **E**||**c**. To overcome this problem many-photon absorption has been used for GaN [7]. In this paper,

however, we show that carefully analyzed polarized photoluminescence spectra give a comprehensive access to the excitonic fine structure of GaN.

Excitonic fine structure

The low-temperature photoluminescence of undoped GaN layers is typically dominated by a strong emission due to excitons bound to an intrinsic donor. This is shown in Fig. 1 for the case of a high-quality GaN epitaxial layer grown on sapphire [6]. The inset Fig. 1(b) gives the luminescence on a linear intensity scale. However, the fine structure in the range of the free exciton is seen much more clearly if plotted on a logarithmic scale as in Fig. 1 (a). The reflection spectrum of the sample shown for comparison allows to identify the emissions due to the decay of A-, B-, and C-excitons. Additional fine structure with high contrast is observed in the range of the excited state n=2 of the A-exciton. On the basis of recent polarized and magnetooptical measurements we identify these structures as due to S and P-states as shown in the figure. From the energy difference between the S states of the n = 1 and n = 2 A-exciton it is possible to determine the binding energy of the A-exciton. This results in a value of 22.3 meV, lower than most results published to date. One should keep in mind that the determination of the binding energy of the exciton using the energy difference between the n = 1 and n = 2 states of the hydrogenic series is not as reliable as that using higher excited states because the effective-mass approximation has only limited validity for the n = 1 state. At this point, however, no higher excited S-states are known in GaN.

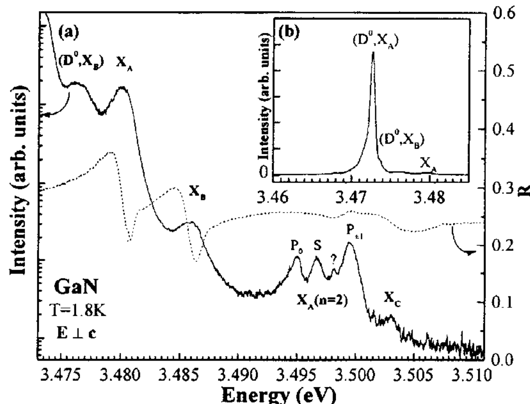

Figure 1: The emission spectrum of free excitons in a 400 μm GaN epilayer exhibits a rich and intensive fine structure (a) beside the very strong and narrow donor-bound-exciton luminescence(b).

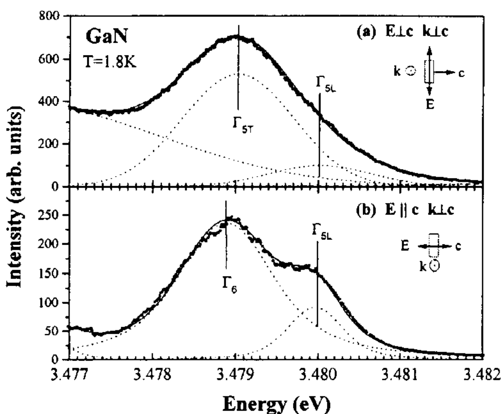

Figure 2: The emission from the n = 1 state of the A-exciton in a free-standing 300 μm GaN epilayer in perpendicular (a) and parallel (b) polarizations allows to determine the LT splitting and the energy of the 'forbidden' triplet exciton.

Figure 2 displays the polarized low-temperature emission spectrum from a side face of a free-standing 300μm thick sample after band-to-band excitation. The recorded data are represented by small squares. To analyze the spectra we performed a fit of the whole excitonic emission spectrum for each polarization. The fitted peaks are simple Gaussian or Voigt lineshapes represented by dotted lines. The sum of the peaks is represented by a full line. It is striking that both spectra are well fitted only by a sum of *two* peaks. A weak underground from the neighboring B-exciton emission on the low-energy side and the stronger donor-

bound B-exciton (D^0,X_B) on the high-energy side was taken into account, cf. Fig.1. While the high-energy peak is seen at the same energy of 3.48000 eV in both polarizations within our experimental accuracy a striking difference is observed between the perpendicular and parallel polarizations in the low-energy peak positions of Figs. 2 (a) and (b), respectively. In the perpendicular polarization this peak is found at 3.47904 eV while in parallel polarization 3.47892 eV are measured. On the basis of a group theoretical argumentation we identify the latter value with the energy 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 is ascribed to the splitting of these states caused by the exchange interaction between electron and hole in the Γ_{5T} state [8]. We assign the peak at 3.48000 eV seen in both spectra to 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 caused by exchange interaction. This value is in perfect agreement with our analysis of reflection data using Pekar's additional boundary conditions [9]. The determined peak positions and the resulting energy splittings are summarized in table 1.It should be noted that even though the thickness of several hundred μm lets us expect bulk properties not influenced by the residual strain due to lattice mismatch slight energy variations of less than 1 meV are still observed between different samples of this type. This is caused by slight variations of the residual strain. Our recent spatially resolved photoluminescence, cathodoluminescence and Raman measurements revealed that the excitonic energy levels strongly depends on the distance from the substrate interface and the impurity concentration at the sample position investigated [10].

The dependence of the peak positions of the A-exciton emissions on magnetic field was again determined by lineshape fits as described above. It is shown in Fig. 3. for **H||c** and **H⊥c**, respectively, for the first time. Group theory predicts for **H||c** a linear Zeeman effect between the two components of each, Γ_5 and Γ_6 states [8]. The splitting of the Γ_5 substrates is governed by the difference of the g-values of electron and hole ($g_e^{\|}$-$g_h^{\|}$) due to their antiparallel spin while the splitting of the two Γ_6 substrates follows the sum, ($g_e^{\|}$+$g_h^{\|}$), as a consequence of the parallel spin of electron and hole. For **H⊥c** a linear Zeeman effect between the Γ_5 and Γ_6 states is expected from group theory governed by $g_e^{\perp}$. The analysis of the data yields the g-values listed in table 1. The Γ_5 states do not exhibit a strong diamagnetic shift in both configurations which we ascribe to a mixing of these states induced by second-order magnetic-field effects. The g-value of 2.0±0.2 for **H⊥c** is in good agreement with the results of other studies [6]. g-values for **H||c** have not been reported before for GaN. It is interesting that we observe a

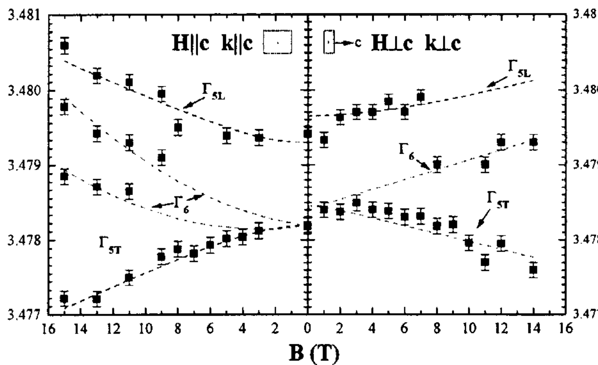

Figure 3: Splitting of the energy levels of the n = 1 state of the A-exciton in GaN in magnetic fields parallel and perpendicular to the c-axis. The Faraday configuration was used.

$g_e^{\|}$	$g_{h,A}^{\|}$	$g_e^{\perp}$	Δ_{LT} (meV)	Δ_{65} (meV)
2.3±0.2	-1.3±0.2	2.0±0.2	0.96±0.1	-0.12±0.1

Table 1: g-values in GaN, finestructure splittings of the n = 1-state of the A-exciton

Zeeman effect between the longitudinal and transverse exciton in a magnetic field. In other wide-gap materials it is quenched by the stronger LT splitting[11].

High-density effects in group-III nitrides

In a previous paper [12] we demonstrated by a lineshape fit that in the region of intermediate excitation density up to 5 MW/cm^2 the radiative decay of biexcitons (M-band) can be the dominating low-temperature emission and gain process in GaN. From the onset of the emission threshold in our lineshape fits we determined the biexciton binding energy in GaN. It amounts to 3.7 meV. This luminescence band M is shown in Fig 4 (a) as a function of excitation intensity for a GaN/SiC epilayer. It exhibits a slight red shift with growing excitation density which is caused by the increased kinetic energy of the biexcitons. The emission spectrum of the same sample at high excitation densities up to 50 MW/cm^2 is given

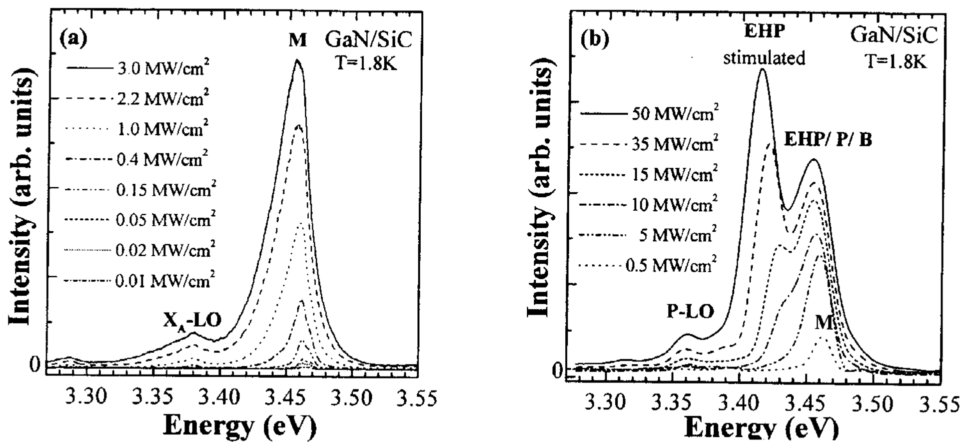

Figure 4: Luminescence from a 3 µm thick GaN/SiC epilayer at intermediate (a) and high (b) excitation densities.

in Fig. 4 (b). Here, the biexciton emission gives way to a superposition of different luminescences caused by inelastic exciton scattering (P), band-to-band recombination (B) and the electron-hole-plasma (EHP). The most striking observation is the appearance of a new emission band around 3.43 eV at 10 MW/cm^2. It exhibits a superlinear growth of emission intensity while strongly shifting its peak position to lower energies. This behavior is typical for stimulated emission from an electron-hole plasma. Similar observations in GaN at low temperatures were made before by Cingolani *et al.* [13]. Wiesmann *et al.* recently showed by room temperature measurements that the observation of this strong peak from the surface of the epilayer is due to scattering of in-plane stimulated emission [14]. With the fast decay of the density of the plasma after the excitation pulse band-to-band recombination, inelastic scattering processes between excitons, and the formation of biexcitons (M) become possible and all give rise to luminescence in the same energy range. The gain measurements presented below will prove this interpretation. Up to room temperature the integrated intensity of the EHP peak follows the predicted T^{-3}-rule [15]. At 270 K the measured peak energy of 3.221 eV is virtually equal to those often reported in the literature for stimulated emission from GaN at room temperature [e.g.,16]. Fig. 5 displays two series of gain spectra taken at various excitation densities (a) and temperatures (b), respectively. The spectra presented here were smoothed to enhance the visibility of the observed spectral features. In the density series of Fig. 3 (a) a broadening of the region of optical gain with increasing pump intensity is observed. Additional structures B and EHP appear on both the high- and low-energy shoulders

of the main peak M. Their relative strengths with respect to M increase with excitation. This main peak is due to biexciton decay below 8 MW/cm^2. Above, inelastic exciton-exciton scattering P is likely to contribute in the same energy range. The low-energy peak EHP can be identified as due to the electron-hole plasma by its energy position and shift characteristics which are identical to those of the stimulated EHP emission shown in Fig. 1. At 30 MW/cm^2 the EHP represents the dominating low-temperature gain mechanism with a peak gain value of 250 cm^{-1}. The high-energy gain peak B appears at energies near or above the band gap of the sample. This peak does not correlate to a pronounced spontaneous emission peak. The zero-crossing energy due to this process shifts to higher values at increased pump intensities. We ascribe this gain peak to band-to-band recombination. The blue shift with increasing pump intensity is typical for this gain mechanism and is caused by a shift of the respective quasi-Fermi levels of holes and electrons into the valence and conduction bands [17].

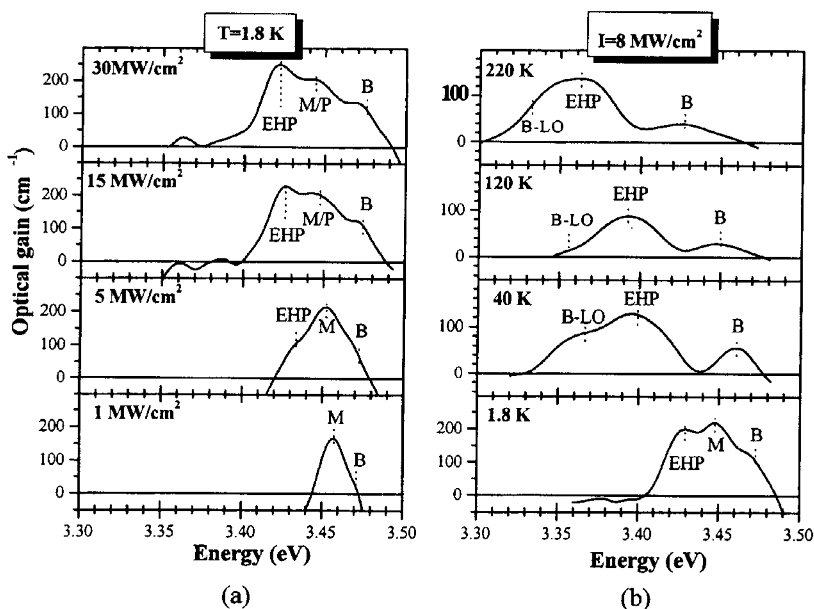

Fig. 5: Optical gain spectra of a 3mm GaN/SiC epilayer (a) at 1.8 K and various excitation densities, (b) at 8 MW/cm^2 and various temperatures.

Our observation of gain caused by plasma, free carriers, and excitonic processes at highest excitation levels does not imply that they all occur simultaneously. In our time-integrated measurements we detect all processes which produce optical gain during and after the excitation pulse. Time-resolved measurements of the optical gain in CdS showed that carrier diffusion as well as the formation of biexcitons and excitons contribute to the ultrashort decay of the plasma within 100-200 ps [18]. It is well known that free carriers at high densities as well as biexcitons and inelastic excitonic scattering processes give rise to optical gain themselves. Thus, our observations are in perfect agreement with the typical behavior observed in other direct wide-gap semiconductors. The temperature-dependent gain measurements of Fig. 3 (b) taken at a fixed excitation density of 8 MW/cm^2 show that below the near-gap gain band a second broad low-energy band appears and grows with increasing temperature. It is this structure that is responsible for the stimulated emission at room temperature. In the high-energy band only band-to-band recombination B can be identified without doubt due to its zero-crossing energy above the band gap of the sample at the

respective temperatures. Since the shape of this gain band is untypical for pure band-to-band transitions excitonic processes probably also contribute to a small extent to the gain in this region at higher temperatures. Inelastic scattering processes between excitons or between excitons and free carriers are typical gain processes at higher temperatures and were observed in thick GaN epilayers before [5]. However, in the thin epilayer investigated here excitonic processes do not play an important role for the gain at high excitation densities and high temperatures. Instead, the electron-hole plasma and LO-assisted band-to-band recombination are the dominating processes causing the low-energy gain band at temperatures above 40 K.

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