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Free Excitons in GaN

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Abstract

Optical spectra on free exciton properties for GaN are presented and discussed, in particular the influence of epitaxial strain and temperature. The exciton-phonon coupling is also manifested via the temperature dependence of the LO phonon replicas of the free exciton.

1. Introduction

Like with most wide bandgap semiconductors excitons play an important role in the optical properties of GaN [1]. The fundamental near bandgap A, B and C-excitons in GaN are connected with the splitting in the valence band top of GaN into the three states Γ_9, Γ_7, and Γ_7 [2] [3]. The energies of A, B and C excitons are quite sensitive to the heteroepitaxial strain in thin layers [4] [5] [6] [7] [8]. This strain is largely understood as due to the difference in thermal expansion coefficients between layer and substrate. The strain will also affect the temperature dependence of the exciton energies [4]. The polariton splitting of the excitonic states has not been spectrally resolved, but the lower polariton dispersion is manifested in the relative intensities of the excitonic photoluminescence (PL) lines and their phonon replicas.

2. Exciton spectra and epitaxial strain.

Low temperature PL spectra for undoped GaN typically show (donor- or acceptor-related) bound exciton (BE) lines as well as the free exciton (FE) lines (A, B and C), provided a sufficiently high dynamics is used in the data collection [6]. Such PL spectra, together with reflectance data for the FE lines, provide accurate values for the exciton energies. Samples of a thickness of a few µm grown on sapphire substrates demonstrate a clear upshift of the lowest A and B excitons by 10-15 meV (depending on the sample), compared to a thick bulk-like GaN sample with a much reduced strain [4] [5] [7] [8] [9] [10] [11] (Figure 1). The upshift for the C exciton is found to be larger than for A and B excitons, up to 30 meV. For growth on SiC on the other hand, a downshift of the excitonic energies is observed. The A and B excitons are typically downshifted about 10 meV compared to a thick unstrained bulk GaN sample, for a sample grown without buffer layer (Figure 1). The broad (4-5 meV) FE peak typically seen in PL from GaN layers grown on SiC without buffer layer is suggested to be a superposition of the A and B excitons (Figure 1), while the second peak observed at higher energies at elevated temperatures in PL (labelled FE_2 in Figure 2b) is attributed to the C exciton [7] [8]. Thus the C exciton is downshifted slightly more than A and B excitons for growth on a SiC substrate (the A-C energy difference in unstrained bulk is measured as about 23 meV [12]). An alternative model assuming that the two excitons seen for GaN/SiC layers are the A, B excitons has recently been proposed, however [13] [14].

These exciton shifts can be explained from the different thermal expansion coefficients of GaN, sapphire, and SiC [4] [15]. The GaN layer grown on sapphire then experiences a compressive biaxial strain upon cooldown from growth, which will increase the exciton energies [16] [17]. For GaN on SiC the situation is reversed, i. e. the GaN layer is under a tensile biaxial strain, which will lead to lower exciton energies [4] [8].

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Homoepitaxial layers of GaN on bulk GaN have recently been produced by MOCVD [18]. These layers have the rather small strain from the difference in lattice constant between the degenerate n-type substrate and the low doped epilayer [18]. The FE energies at 2 K reported from such layers are A = 3.478 eV, B= 3. 483 eV and C = 3.502 eV, in good agreement with recent data from very thick GaN layers [1] [12].

The free A exciton binding energy has recently been estimated as about 27 meV in unstrained GaN (26.8 meV was reported in Ref 12). It is not established how this value varies with strain. Recent experimental data appear conflicting. Some very low values for the binding energy of A in GaN layers grown on sapphire (18 meV and 20 meV, respectively [19] [20] [21]), could be due to an incorrect labelling of the excitonic peaks, i. e. the donor bound exciton peak was mistaken for the A peak [19] [20] [21]. The donor bound exciton is typically quite strong in PL spectra even in rather pure samples (<10^{17} cm^{-3}). Comparison with reflectance data are important to avoid misinterpretations; only the free exciton features are strong in reflectance [2] [3] [5] [12]. The A binding energy is indeed expected to be around 27 meV in strained epilayers, possibly slightly larger on sapphire, and slightly smaller on SiC.

3. Temperature dependence of exciton spectra.

The excitonic PL peaks can be followed up to higher temperatures. In Figure 2 is shown a set of PL curves for a double heterostructure AlGaN/GaN/AlGaN sample grown on sapphire. This type of structure gives a much higher radiative efficiency at elevated temperatures, compared to single GaN epilayers where the bare GaN surface is excited in the PL measurement. The PL is dominated by the Si donor bound exciton emission below about 50 K. At higher temperatures the A and B free excitons dominate the PL spectra. There is no shift over to a band-to-band transition in the temperature range studied (up to 300 K). Such a transition would be manifested by the occurrence of a new peak at about 25-30 meV higher energy than the A exciton, and this peak is expected to gradually take over the main PL intensity at the expense of the excitonic transitions. Obviously this does not happen in the spectra shown in Figure 2, indicating that low doped GaN has an excitonic behaviour up to room temperature. This is consistent with the strong excitonic peak seen in absorption of GaN at room temperature [22]. In Figure 2b is shown a similar collection of PL spectra for the case of GaN grown on SiC. The behaviour of the lowest energy intrinsic PL peak is similar to the case in Figure 2a, i. e. we conclude that the FE recombination dominates the PL up to room temperature.

The phonon coupling of the free exciton transitions is related to the exciton-polariton coupling [23] [24] [25]. The relative strength of the phonon replicas is a measure of the phonon scattering needed to get across the bottleneck in the lower exciton-polariton branch over to the radiative branch of the dispersion curve [25]. A linear temperature dependence of the 1LO / 2LO intensity ratio of the FE PL is expected in the temperature range below say 100 K [23]. This is also observed in our temperature dependent PL spectra on GaN (Figure 3a and Figure 3b), and this supports the classical exciton-polariton model for the excitons in GaN. Another observation in Figure 3 is the relatively strong intensity of the no-phonon line, in comparison with the 1LO- and 2LO-phonon replicas. This effect points to an enhanced scattering rate of the exciton polariton into the radiative branch of the no-phonon A-exciton. One possible explanation would be that the high defect density (point defects, residual dopants, and dislocation defects) plays a role in the polariton scattering, assisting in the momentum transfer. More data on samples with a lower defect density than available for this work are needed to definitely clarify this question, as well as to resolve spectrally the exciton-polariton splitting in GaN. A polariton splitting of about 1-2 meV would be expected for GaN, i e of comparable magnitude as for CdS.

4. Temperature shifts of exciton energies.

The temperature shifts of the A exciton energies are very different for the strained layers grown on sapphire, compared to unstrained bulk GaN. The GaN grown on sapphire has a much larger temperature shift, while the corresponding shifts for GaN grown on SiC are quite small (see Figure 4). Therefore the exciton energies for the samples studied differ much less at room temperature than at liquid helium temperatures. These strong strain effects on the temperature dependence of exciton energies have been ignored in recent literature, where discussions on the physical background of this temperature dependence were presented [10] [26].

The general trend for the heteroepitaxial layers illustrated in Figure 4 is understood from the differences in the thermal expansion coefficients, if it is assumed that the strain energy below room temperature has to be accomodated elastically. From measurements of the lattice parameters from these samples it is clear, however, that the thin layers grown on sapphire and SiC in Figure 4 are both strained at room temperature. We find e g typical c-values for GaN on SiC as 5.182 Å, as compared to the unstrained value 5.1855 Å. Using AlN buffer layers the epitaxial strain can be reduced, as seen in microstructure analysis [27]. An MBE-grown GaN buffer layer apparently has a similar effect on strain reduction, as evidenced from the peak position in PL spectra [28]. There are reports in

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literature that GaN grown on sapphire with an AlN buffer layer are essentially unstrained at room temperature [29]. This was not the case in the layers studied by us. It may be assumed that the detailed cooling cycle during cool down from growth may influence the strain relaxation via dislocation defect reactions, leading to a different residual strain at room temperature in different layers.

To explain the detailed behaviour of the exciton energies as a function of temperature it is necessary to know the full strain tensor, and in addition the corresponding deformation potentials for the induced shifts of exciton energies [30]. The detailed temperature dependence of the thermal expansion coefficients also needs to be considered. These may not be known accurately, since literature values for GaN are conflicting [15] [31]. The strain situation for a layer at a particular temperature depends on the details of the grown structure (number of layers and their thicknesses, as well as on type of substrate), whether strain relaxation is complete at the growth temperature, the cool down procedure (i. e. whether there is sufficient time for strain relaxation during cool down), presence and thickness of buffer layer, and also to some extent the doping and point defect densities, since these do influence the lattice parameters [32]. Obviously data for a good pure bulk GaN sample are needed for reference before data like those in Fig 4 can be fully understood.

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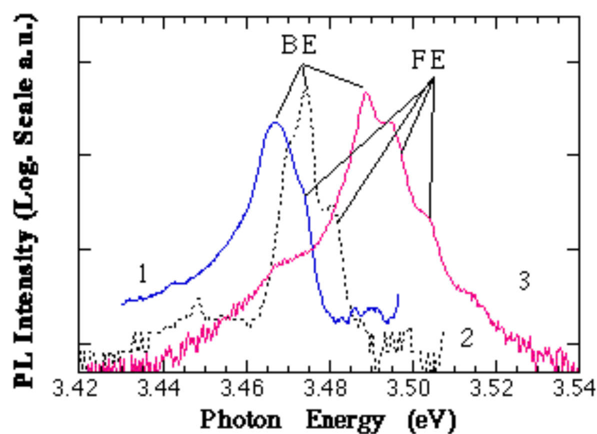

Figure 1. Photoluminescence spectra at 2 K for three GaN samples: two epilayers grown with MOCVD on sapphire with AlN buffer layer (3) and SiC without buffer layer (1), respectively, and for comparison a 500 µm thick HCVD grown bulk-like layer (2). These spectra are obtained with low spectral resolution (about 5 meV).

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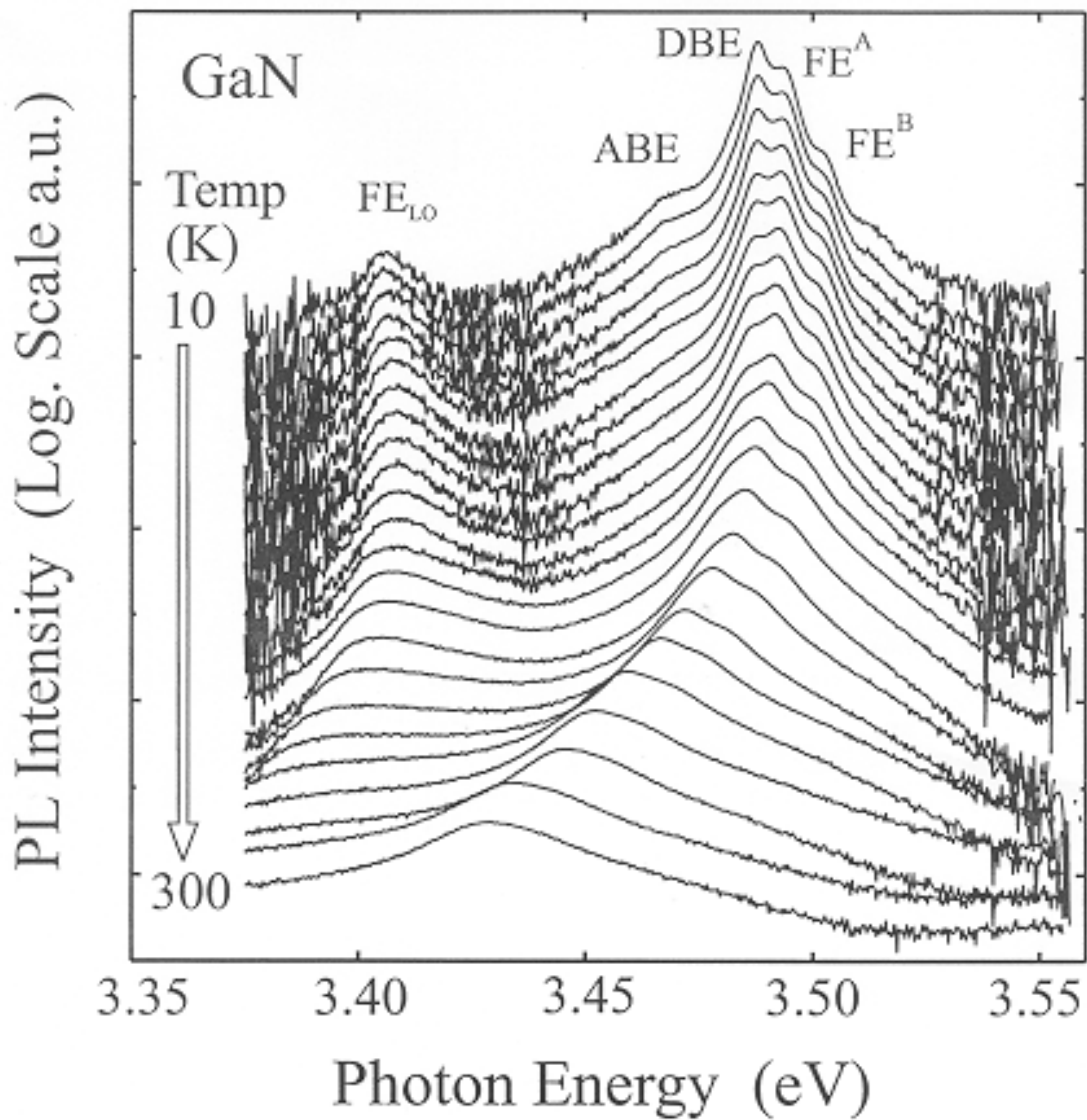

Figure 2a. Photoluminescence spectra at different temperatures for a GaN layer with AlGaN barriers grown with MOCVD on sapphire. The approximate temperatures are (from top): 10 K, 20 K, 25 K and with interval 5 K up to 60 K; interval 10 K in the range 60 K to 100 K; interval 20 K between 100 K and 300 K.

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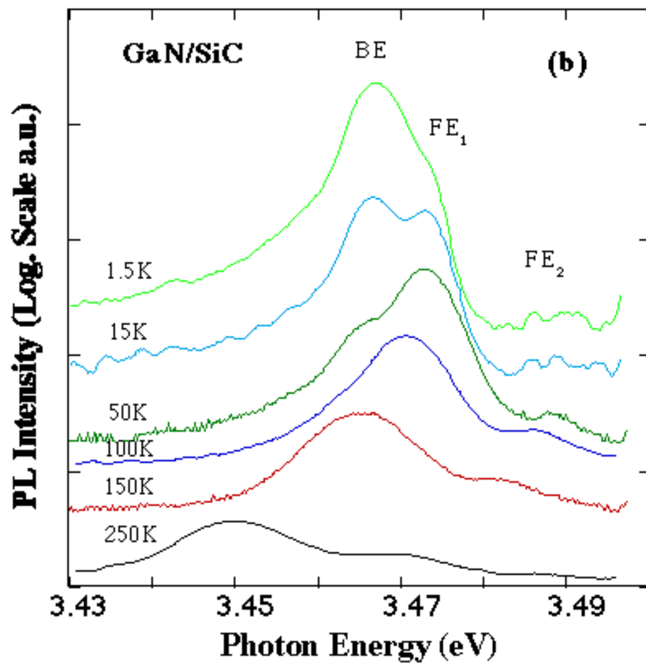

Figure 2b. Photoluminescence spectra at a set of different temperatures for a GaN layer grown with MOCVD on 6H-SiC without buffer layer (same as sample 1 in Figure 1).

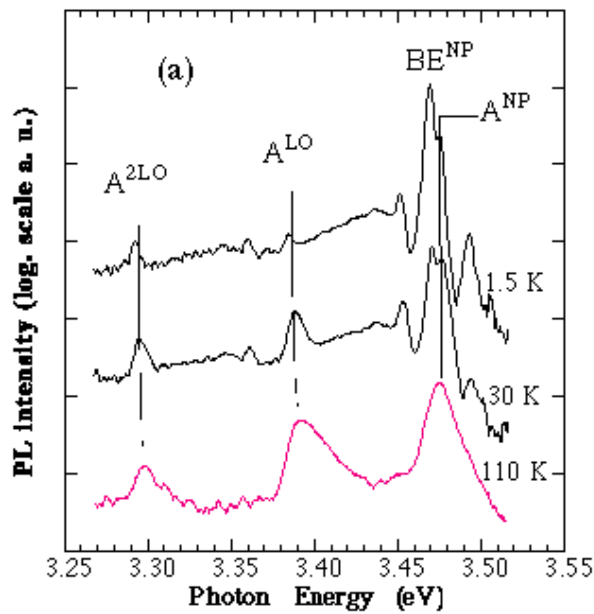

Figure 3a. Photoluminescence spectra at different temperatures for a 500 µm thick HCVD grown GaN sample, showing the temperature variation of the LO replicas of the A exciton.

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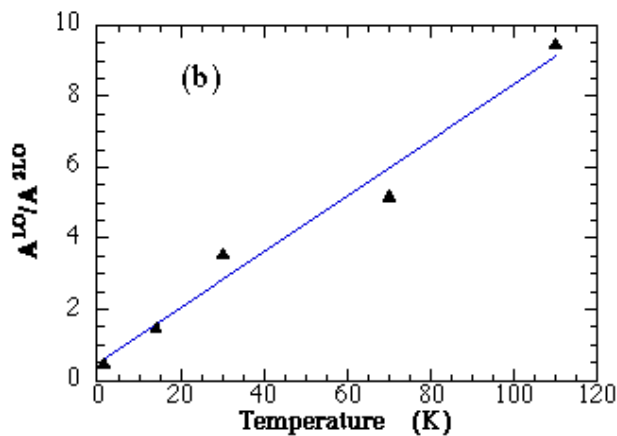

Figure 3b. Plot of the intensity ratio between the 1LO and 2LO replicas for the free A exciton at different temperatures (data from Fig. 3. a.).

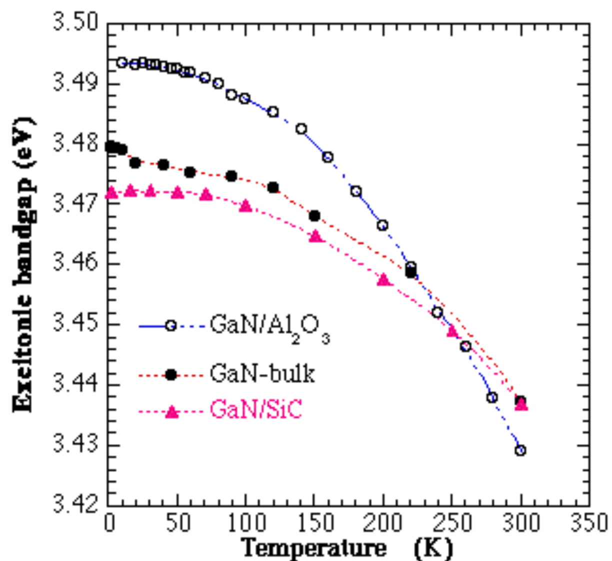

Figure 4. Temperature dependence of the free A exciton energies from photoluminescence data in three different samples (same as in Figure 1.).

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