SELECTIVE DYNAMICAL STUDY OF LUMINESCENCES NEAR THE SURFACE AND THE INTERFACE OF EPITAXIAL GaN

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ABSTRACT

Recombination processes and their dynamics are selectively studied (a) near the interface betweeen a 400µm thick GaN epilayer and its Al_2O_3 substrate and (b) in the structurally relaxed regions near the surface of this sample. Strong radiative excitonic recombination is observed in the relaxed regions. However, the recombination dynamics of free and shallow-bound excitons here are strongly influenced by shallow and deep defects. Near the substrate the presence of dislocations suppresses radiative recombination of free and shallow bound excitons. Deeper emissions appear which we attribute to excitons deeply bound to dislocation-related defects. They exhibit ps-recombination dynamics effected by strong nonradiative contributions.

INTRODUCTION

The now demonstrated use of the InGaAlN alloy system over most of the visible spectrum makes it one of the key materials for future optoelectronical applications. Among the major research issues at this point is the development of a GaN-based blue laser diode. Present light-emitting diodes use an impurity related recombination process [1] and exhibit excellent performance despite a dislocation density as high as $10^9\,cm^{-2}$ [2]. For laser action sufficient gain is expected to rely on an intrinsic recombination process involving free carriers or excitons. Present growth techniques using mismatched substrates cannot prevent the creation of dislocations and defects near the interface nor the incorporation of the intrinsic shallow donor 35 meV below the conduction band edge. It is therefore necessary to assess the influence of impurities and dislocations on the excitonic recombination processes and their dynamics in GaN.

The present paper will show that the dominating recombination processes near the interface between GaN and its lattice-mismatched substrate differ strongly from those far away from the interface, i.e., near the surface of the epilayer. We will show that in structurally perturbed regions such as in the vicinity of the interface, the radiative recombination of free and shallow bound excitons is quenched and deep dislocation excitons appear in the spectrum. A detailed report on the recombination dynamics both near and far away from the interface will be given.

EXPERIMENTAL

To separate the influence of the dislocations having a high density near the substrate interface from the properties of relaxed single-crystalline GaN we used in the main an epitaxial GaN layer of 400µm thickness grown by hydride vapor phase epitaxy without a buffer layer [3]. Using band-to-band excitation from either the epilayer side, or the substrate side we sampled without any overlap either high-quality, relaxed GaN near the surface or strongly perturbed GaN near the interface. Due to the high absorption coefficient above the gap, the estimated depth of excitation within the sample is less than 5 µm. We therefore use the terms 'bulk' and 'interface'

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luminescence to distinguish between excitation from either the epilayer or the substrate side. The sapphire substrate is transparent at the energies of excitation and detection and does not influence the spectrum taken from the interface region. For continuous-wave (cw-) measurements a HeCd laser was employed. Time-resolved measurements were performed at various temperatures using a frequency-doubled dye laser synchronously pumped by an actively mode-locked and frequency-doubled Nd:YAG laser. The overall time resolution employing convolution techniques was 15 ps.

RESULTS

'Bulk' and 'Interface' Photoluminescence

Comparative cw low-temperature photoluminescence spectra taken from the 400 μm GaN epilayer are shown in Fig. 1. The spectrum in Fig. 1 (a) was obtained after excitation of the sample on the surface of the epilayer. The donor-bound-exciton line I_2 at 3.4782 eV is most prominent. Emission from the free A-exciton is seen at 3.4800 eV. The localization energy of the exciton at the donor thus amounts to 7.18 meV. High resolution spectra reveal the presence of a weak second donor-bound-exciton line with a localization energy of 3.6 meV. The energy positions of the free exciton and I_2 agree precisely with calorimetric reflection and absorption data taken from the same sample [4] and thus unambiguously determine the low temperature energy positions of the free and bound excitons in relaxed GaN. The linewidth of I_2 amounts to 920 μeV, a value that confirms the high quality of HVPE-grown 'bulk' GaN and its potential for a lattice-matched substrate material. Due to the high intensity of I_2, the spectrum on its low-energy side has to be multiplied by a factor of 40 in the spectrum of Fig. 1 (a) to make manifest an acceptor bound exciton line I_1 at 3.446 eV. The other emissions are due to phonon-assisted decay of excitons except for the line at 3.26 eV which is of unknown origin. Donor-acceptor-pair recombination can be excluded because of missing characteristic phonon replica.

The spectrum obtained after excitation of the epilayer through the sapphire substrate at the same excitation density (Fig. 1 (b)) differs very much from that just described. No free and shallow-bound-exciton luminescences are observed here. Instead we see a complex structure of lines between 3.37 eV and 3.31 eV which at higher excitation densities reveals even more lines down to 3.29 eV, see Fig. 4. These lines were already observed in hexagonal epilayers on SiC [5], and also cubic samples on GaAs [6, 7], all grown without buffer layer. The fact that they were observed in samples on various lattice-mismatched substrates indicates that they are an inherent property of structurally disturbed GaN. We see that here the free and shallow bound excitons decay entirely

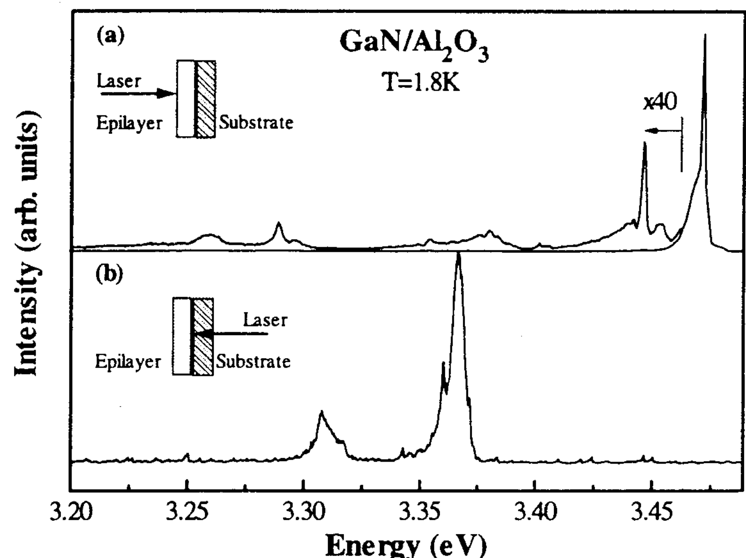

Fig. 1: Low temperature cw-photoluminescence spectra of a 400μm epitaxial GaN/Al_2O_3 layer. (a) 'bulk' luminescence excited from the epilayer side, (b) 'interface' luminescence excited through the substrate.

nonradiatively. We attribute the observed 'interface' emissions to the annihilation of excitons deeply bound to defect centers connected with dislocations. The excitonic character of these lines will become clear below. Dislocation excitons are well known in other materials like CdS [8, 9]. Beside these dislocation excitons a broad emission band at 2.4 eV is also observed [10].

Summarizing the results of the cw-spectra, we see that far away from the substrate HVPE GaN exhibits strong radiative recombination at low temperatures due to free and shallow bound excitons. On the other side, in the presence of defects and dislocations near the substrate, the decay of free and shallow bound excitons is completely nonradiative. The excitation energy is transferred to deep levels associated with defects and dislocations localized near the interface, giving rise to emissions between 3.37 eV and 3.31 eV.

In the following section the dynamics of the energy relaxation of free and shallow bound excitons and of the deeply bound dislocation excitons will be investigated.

Recombination Dynamics in 'bulk' GaN: Free and Shallow bound Excitons

In the previous section we showed that free and donor-bound excitons contribute to strong radiative recombination in high-quality GaN at low temperatures. To get a better picture of the influence of nonradiative processes it is necessary to increase the temperature. We observed a rapid decrease of the intensity of the donor-bound exciton with raised temperatures governed by an activation energy of 7 meV. This value agrees very well with the localization energy of the exciton at the shallow donor. The physical process involved is the dissociation of the exciton from the donor caused by the absorption of low-energy acoustical phonons which are present even at relatively low temperatures. We will now show that this process also governs the recombination dynamics of the donor-bound exciton. In Fig. 2 (a) luminescence transients of the shallow-donor-bound-exciton line after band-to-band excitation are shown for different values of the lattice temperature. 'Bumps' in the very fast transients are caused by the response of our detection system to ps-signals and do not have any physical meaning. No rise process can be resolved in any transient from which we have to conclude that the lifetime of the free exciton is shorter than our time resolution of 15 ps at low temperatures. The lifetime of the donor-bound exciton of 70 ps at 8 K is seen to decrease con-tinously with increa-sing temperature, corresponding well to the expected increa-sed dissociation rate as was also reported by Chen et al. [11]. How does

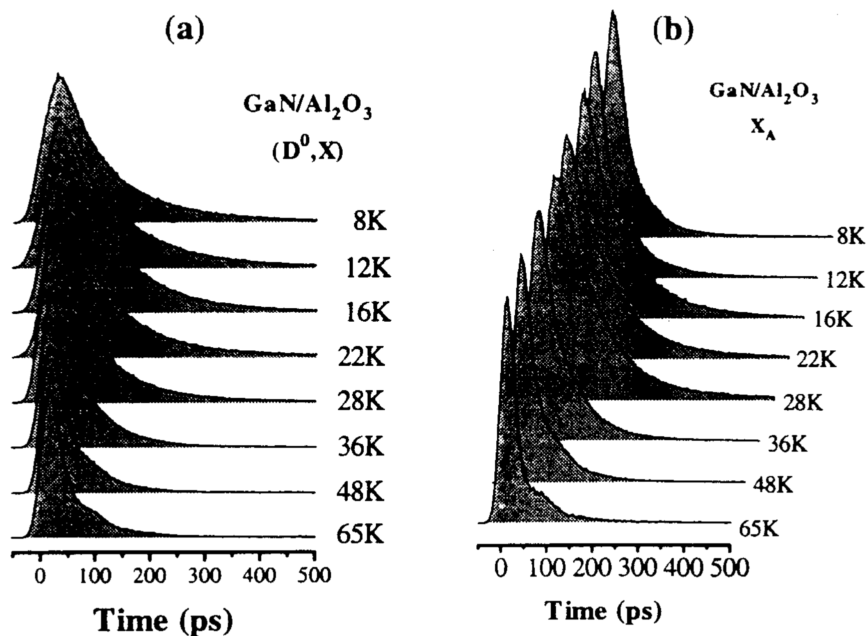

Fig. 2: Luminescence transients (a) from the donor-bound exciton (D^0,X) , (b) from the free A-exciton X_A, , taken at different lattice temperatures after excitation from the epilayer side ('bulk' luminescence).

this increased dissocia-tion affect the transients of the free exciton? The answer is given in Fig. 2 (b). At low temperatures the decay is fast as expected from the lack of a rise process in the bound-exciton transients. As soon as the donor-bound exciton decay becomes faster with increasing temperature, the luminescence transient of the free exciton slows down. Above 28 K the free exciton decay becomes again faster.

To prove that the dissociation of the bound-exciton from the donor is responsible for this temperature dependence of the free-exciton transient, we evaluated a three-level model with temperature-dependent transition probabilities, Fig. 3 (a). Corresponding to our experimental excitation conditions we assume the system to be in the free-exciton state initially. Here we neglect the comparatively short exciton formation time. We also assume that the only temperature-dependent process is the thermally activated dissociation of the bound exciton from the donor, given by the characteristic time constant τ_{23}, cf. Fig. 3 (a). Its temperature dependence is set as

$$\tau_{23} = \tau_{23}^{\infty} \cdot \exp(\Delta E / kT) \qquad (1)$$

ΔE denotes the localization energy of the exciton at the shallow donor, k Boltzmann's constant and T the lattice temperature. The decay rate of the free exciton is assumed to be independent of the lattice temperature. The solution from the two coupled rate equations was used to model luminescence transients by convolution with the response of our detection system to the laser pulse, see Fig. 3 (b). The effects observed in the experiment are nicely reproduced by the calculated transients even though a perfect fit has not been achieved. We ascribe the difference between the measured and calculated transients to the effect of the second donor-bound exciton with 3.6 meV localization energy. However, the parameters used in the calculation of the transients, which give the closest resemblance to the observed temperature behaviour, are shown in Fig. 3 (b) and serve as a reasonable estimate of the actual transition times. We see that not

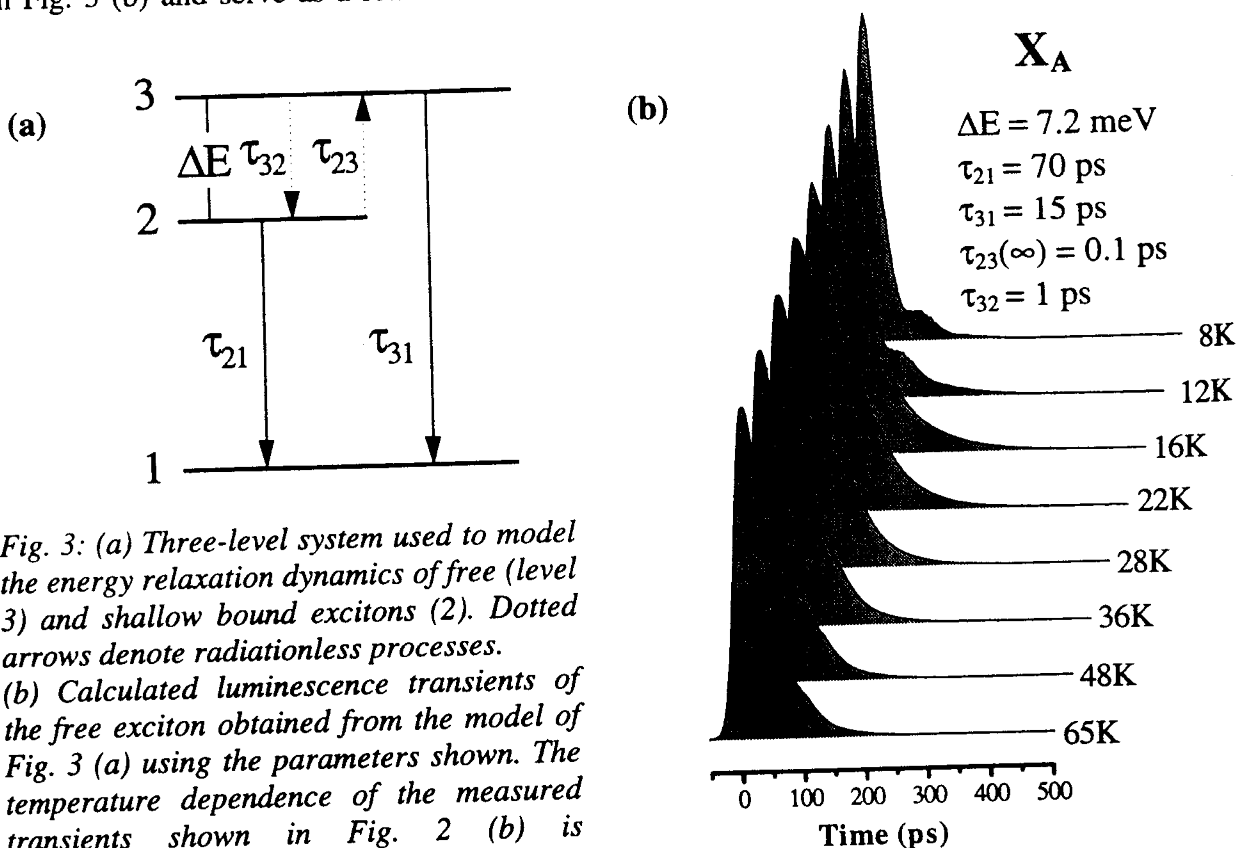

Fig. 3: (a) Three-level system used to model the energy relaxation dynamics of free (level 3) and shallow bound excitons (2). Dotted arrows denote radiationless processes.
(b) Calculated luminescence transients of the free exciton obtained from the model of Fig. 3 (a) using the parameters shown. The temperature dependence of the measured transients shown in Fig. 2 (b) is qualitatively reproduced.

only the decay time τ_{31} describing the annihilation of the exciton is short in comparison with free exciton lifetimes in other high-quality materials such as CdS, but also that there is a strong influence of the shallow donors which capture free excitons at low temperatures within 1ps.

To summarize of the results on free and shallow bound excitons in structurally relaxed regions of GaN, through an analysis of the temperature dependence of the luminesence transients we obtained an estimate of the time constants governing the energy relaxation in this energy range. We observe a fast luminescence decay of the free exciton which is additionally accelerated at low temperatures by the capture at the shallow donor. Further nonradiative relaxation processes have to be taken into consideration to account for the short exciton decay time τ_{31} of less than 15ps. The observation of transition metals in this sample which are known to act as 'luminescence killers' is a likely explanation [12].

Recombination Dynamics near the Substrate Interface: Deeply Bound Excitons

We performed a comparative study of the recombination dynamics of emissions between 3.29 eV and 3.37 eV in various samples grown by HVPE or MOCVD. We find that the results agree with our previously reported measurements on GaN/SiC [5], showing again that these emissions are a general feature of disturbed GaN. The time constants vary only slightly between different samples. As an example, the results obtained from a thinner GaN/SiC epilayer is summarized in Fig. 4, which also gives a spectrum using pulsed excitation. Lines are marked L_1 to L_8 with increasing energy. As also observed by Hong et al. [7] the shoulder at 3.360 eV observed in Fig. 1 (b) develops into a well resolved line L_7 given higher excitation densities. Also, additional lines L_1 and L_2 at 3.28 and 3.29 eV are detected at higher excitation densities. The luminescence decay in the whole range is fast with time constants in the ps-range. It can be fitted using one or two exponential decays. The spectral analysis of the decay shows that transients with two time constants are always caused by the spectral overlap of different

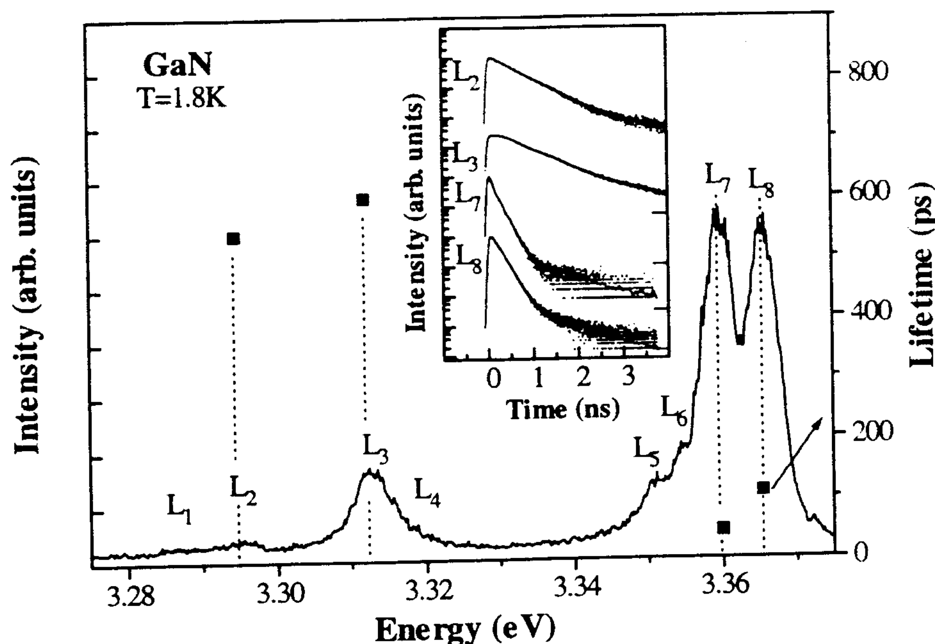

Fig. 4: Luminescence spectrum of deeply bound excitons in GaN at higher excitation densities effected by ps-laser pulses. The filled squares denote the decay constant (right scale) at the respective energy positions. In the inset the pertaining luminescence transients are shown. Here dotted curves stand for the experiment while full lines represent two-exponential fits.

luminescences. Thus, the decay of each luminescence is essentially monoexponential. On the basis of this result, donor-acceptor-pair recombination as suggested by some groups [7, 13] for the 3.311 eV line can be excluded as interpretation of this luminescence. Due to the energy position close to the band gap and the monoexponential luminescence decay we attribute the lines observed to excitonic recombination at dislocations. The decay constants in the ps range are unusually fast for a localization energy of more than 100meV and suggest strong nonradiative contributions to the recombination process. Electron-phonon coupling and Auger processes probably add to the short lifetimes observed.

CONCLUSIONS

In conclusion, we compared recombination processes and their dynamics in single-crystalline GaN near the surface of a thick epilayer with those of structurally disturbed GaN near the interface to the lattice mismatched substrate. We observe strong, radiative excitonic recombination due to free and shallow bound excitons near the surface. However, the decay of the free exciton is fast due to the impact of deep impurities. It slows down at temperatures between 20 K and 40 K where thermally activated dissociation of shallow bound excitons contributes to the free-exciton population. Near the substrate the presence of dislocations supresses the radiative decay of free and shallow bound excitons. Instead, we observe characteristic emissions between 3.31 and 3.37 eV whose decay is fast and monoexponential strongly suggesting that they are caused by dislocation excitons.

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