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Field-dependent charge carrier dynamics in GaN: Excitonic effects

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The electric-field dependence of the charge-carrier dynamics in GaN was studied by measuring excitation spectra of the sub-band-gap (yellow) luminescence as a function of bias using a Schottky junction formed at the interface between the semiconductor and an electrolyte solution. At large bias, the contribution of free electrons and holes to the photoluminescence is significantly reduced due to the dead-layer effect. As a result, striking features are revealed in the spectra close to the fundamental absorption. These features are attributed to exciton decay via yellow luminescence centers. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1779349]

Electrons and holes, generated by light within the depletion layer of a Schottky diode, are effectively separated by the electric field and the minority carriers are collected at the interface. Minority carriers created within a diffusion length of the inner edge of the depletion layer can also reach the junction;[1] if they are transferred across the interface one observes photocurrent in the external circuit. Only those carriers created by light with a penetration depth $(1/\alpha)$ which is larger than the sum of the minority carrier diffusion length L and the thickness of the space charge layer W will recombine, either nonradiatively or radiatively. The intensity of the emitted light I_{PL} is given by:[1–4]

$$I_{PL} = \frac{\kappa \phi_0}{1 + \alpha L} \exp(-\alpha W), \quad (1)$$

where ϕ_0 is the absorbed photon flux and κ is the ratio of the rate of radiative recombination to the total recombination rate. Many systems have been shown to conform to the "dead-layer model."[2–4]

Among the III–V semiconductors GaN is rather exceptional in that its exciton binding energy is large ($\geq$25 meV).[5–8] The formation of strongly bound electron–hole pairs might be expected to influence the charge-carrier dynamics within the space-charge layer of an illuminated Schottky diode. In the present work we have used photoluminescence and photocurrent measurements on the Schottky junction formed at a semiconductor/solution interface to study excitonic effects in the field-dependent dynamics of carriers in *n*-type GaN epitaxial layers. We report an anomalous peak in the onset of the excitation spectrum of the sub-band-gap luminescence indicating enhanced emission at large band bending. We argue that this effect is due to a contribution from exciton absorption which is observed because of two reasons: the large binding energy of excitons and the suppression of emission from free carriers as a result of the dead-layer effect.

The GaN epitaxial layers were grown by MOCVD on sapphire substrates using a 30 nm AlN buffer layer to reduce stress.[9] The layers were co-doped with Si. The density of uncompensated donors was 6×10^{17} cm^{-3}. Ohmic contacts were deposited by microwave sputtering of Ti/Al/Ni/Au (15/300/40/200 nm). The (0001) Ga-terminated surface was exposed to solution.[9] A standard three electrode cell was used for the electrochemical experiments. All potentials are reported with respect to the standard calomel electrode. Reproducible clean electrode surfaces were obtained by dipping in HCl before each experiment. The electrolyte for all measurements was 0.5 M H_2SO_4 in water. Electrical impedance measurements were performed using a PAR283 potentiostat and a Solartron SI1255 frequency response analyzer. Photoluminescence excitation measurements were performed using a Jobin-Yvon SPEX 1680 spectrofluorometer.

Two main features are observed in the photoluminescence emission spectrum of the GaN samples. A peak at 3.4 eV is due to recombination of (donor-bound) excitons[8,10] or a band–band transition[11]. A strong band, with a maximum at 2.2 eV is usually referred to as the "yellow luminescence."[11,12] The origin of this band gap transition is still the subject of speculation.[13–16] It is most likely due to defects caused by the Si-dopant[16,17] or unintentional O.[16] In our samples the intensity of this line is strong. In the present work we use this yellow luminescence as a probe for absorption processes. In low temperature absorption measurements three exciton lines (caused by three offset valence bands in wurtzite semiconductors) are observed.[18] When the temperature is raised the exciton lines broaden and, at room temperature, are hidden by the fundamental band-band absorption.

The GaN/electrolyte interface showed typical diode characteristics. Under reverse bias a low blocking current of approximately 100 nA cm^{-2} was observed at potentials more positive than -0.5 V. In this potential range illumination with supra-band-gap light gave an anodic photocurrent, whose potential dependence was in accordance with $j/e\phi_0 = 1-\exp(-\alpha W)/(1+\alpha L)$,[1] or essentially, $1-I_{PL}/\kappa\phi_0$ [see Eq. (1)]. From these results a hole diffusion length L of about 10 nm was estimated. The photocurrent was due to oxygen evolution. Impedance measurements under depletion conditions gave, in a wide potential range (0.0–2.0 V), linear Mott-Schottky plots with only slight frequency dispersion. The free carrier density calculated from the slope (6×10^{17} cm^{-3}) was close to that specified by the growers. The flatband potential V_{fb} was found to be -0.8 ± 0.05 V; this value is in good agreement with the results of Kocha *et al.*[19]

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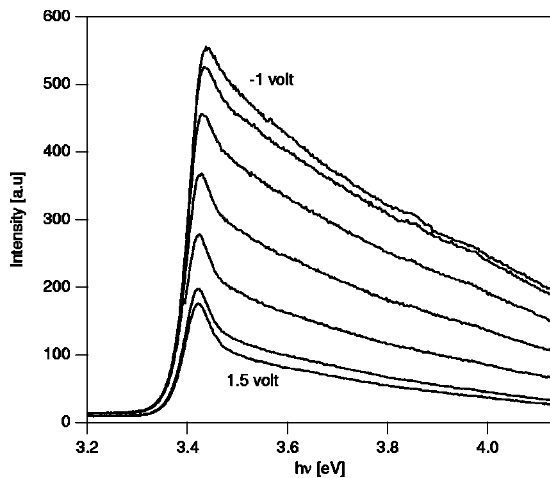

FIG. 1. Photoluminescence excitation spectra as a function of applied potential. The emission was monitored at 2.2 eV. Spectra are shown (from uppermost spectrum on down) at −1, −0.5, −0.4, −0.3, −0.25, 0.5, and 1.5 V, respectively.

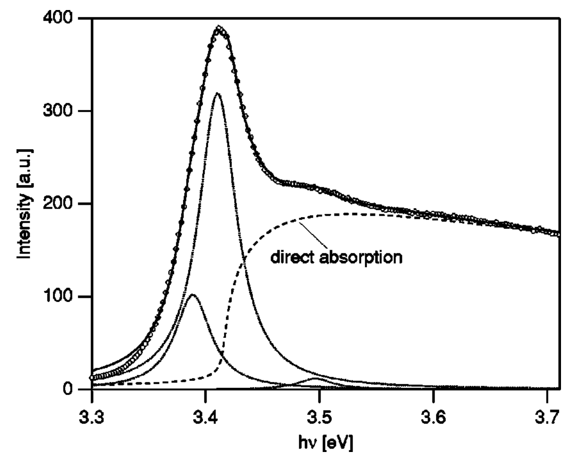

FIG. 2. Fit of the *in situ* photoluminescence excitation spectrum at an electrode potential of 1 V. The positions of the exciton transitions and the band–band transition are indicated. The continuous line through the data points (open circles) is a fit to Eq. (2). The dashed line shows the contribution of direct excitation and the dotted lines show the excitonic peaks.

The emission intensity I_{PL}, measured at 2.2 eV, for an excitation energy of 4.0 eV is low at positive potentials [large W, Eq. (1)] and tends to a maximum value $I_{\mathrm{PL,max}}$ as the potential becomes negative ($W \rightarrow 0$). Since the flatband potential and effective doping density are known, the depletion layer width W can be calculated as a function of applied potential.[20] A plot of $\ln(I_{\mathrm{PL}}/I_{\mathrm{PL,max}})$ versus W (not shown) is linear, confirming the validity of the Gärtner model [Eq. (1)] for this material.

Excitation spectra of the yellow luminescence are given in Fig. 1 for various values of the applied potential. All spectra show an onset at about 3.35 eV, followed by a maximum at about 3.44 eV and a strong decrease at higher photon energy. The spectra depend only slightly on potential in the range −1.0 to −0.5 V (i.e., close to the flatband value at −0.8 V). At more positive potentials—corresponding to depletion—a marked decrease in emitted intensity is observed. In addition, at large band bending a sharp peak develops in the spectra in the onset range at around 3.42 eV.

Photons with an energy much larger than the band gap (≈3.41 eV) generate free electrons and holes. Two variables are important for determining the shape of the excitation spectra in this range: the penetration depth of the light (which depends onthe photon energy) and the thickness of the charge separation layer $W+L$. At negative potentials (close to the flatband condition) minority carriers generated within a diffusion length of the electrolyte interface can undergo nonradiative surface recombination. Electrons and holes generated beyond this region give rise to luminescence. Since the penetration depth of light decreases with increasing photon energy, the emission also decreases markedly. At more positive potentials the electric field in the space charge region plays an important role in separating the electrons and holes, thus giving rise to photocurrent and reducing the emission intensity (the Gärtner model).

Exciton absorption is expected to be important in the onset of the excitation spectrum. Our results suggest that the peak in the spectrum, most pronounced at positive potentials, is due to direct exciton decay at defect sites giving yellow luminescence. The result indicates that, while recombination of free charge carriers can be effectively suppressed by the electric field of the depletion layer, radiative recombination due to exciton relaxation is less sensitive to the electric field present in the depletion layer. Relaxation of the exciton at defect centers must compete effectively with ionization followed by fast separation of the electron–hole pair. It is interesting to note that Liu *et al.*[6] report a pronounced peak in the photovoltage spectrum of a GaN solid state device. They also attribute the peak to excitonic absorption.

To model the system, the separate contributions of band–band absorption and excitonic absorption to the emission intensity are calculated. The absorption due to band–band processes is given by[6,21] $\alpha_{\mathrm{dir}} \propto \mathrm{Real}((E-E_g+\boldsymbol{i}\Gamma_{\mathrm{gap}})^{1/2})$ in which E_g is the band gap of the material, Γ_{gap} is a temperature-broadening factor or tailing parameter, and $\boldsymbol{i}=\sqrt{-1}$. Absorption by excitons is described by a Lorentzian line-shape,[6,21] $\alpha_{\mathrm{exciton},i} \propto 1/((E-E_{\mathrm{exc},i})^2+\Gamma^2_{\mathrm{exc},i})$, in which $E_{\mathrm{exc},i}$ is the energy of the exciton, and $\Gamma_{\mathrm{exc},i}$ is it's temperature-broadening factor. From Eq. (1) and the thickness d of the GaN layer, it follows that the luminescence intensity is given by

$$I_{\mathrm{PL}} \propto \sum_i c_{\mathrm{exc},i}\alpha_{\mathrm{exc},i} + [1 - e^{-\alpha_{\mathrm{dir}}d}]e^{-\alpha_{\mathrm{dir}}(W+L)}. \qquad (2)$$

Figure 2 shows that a fit of a photoluminescence excitation spectrum to Eq. (2), using contributions from three excitons, is excellent from 3.35 to 3.7 eV. Above this energy the fit deviates from the measured values, probably due to the extra transition that is known to occur in GaN at around 4 eV.[5] Below 3.35 eV, the fit is less satisfactory because reflection and interference effects are not taken into account.

From the fit to Eq. (2) the binding energy of the lowest energy exciton ($E_g-E_{\mathrm{exc},1}$) is determined to be 27±5 meV. This value is in accordance with the literature value of around 25 meV,[6–8] illustrating the amenability of the presented method to study excitonic effects in semiconductors even at room temperature. The broadening parameters $\Gamma_{\mathrm{exc},i}$ for all three exciton peaks are about 20 meV which is also in agreement with literature values.[22]

In the current model it is assumed that excitonic contributions to the spectral response do not depend on the electrode potential. This is however not entirely the case. Figure 3 shows the integrated intensity from the excitonic peaks, obtained by fitting the spectra to Eq. (2). At potentials in the vicinity of V_{fb} the contribution of the excitonic process is

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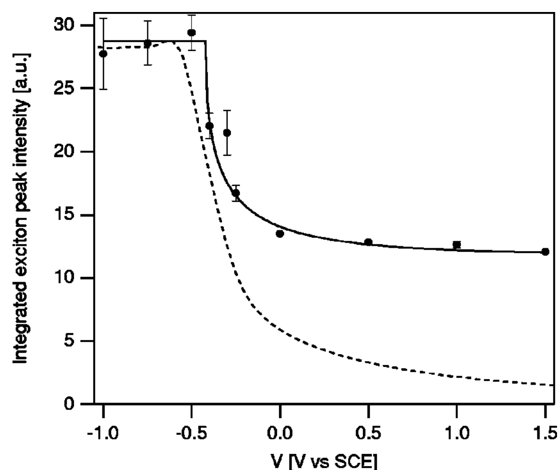

FIG. 3. Integrated intensity of the exciton peaks [obtained by fitting the spectra shown in Fig. 1 to Eq. (2)] as a function of applied potential. The potential dependence of the yellow luminescence under excitation with 4.0 eV light is shown as a reference using a dashed line.

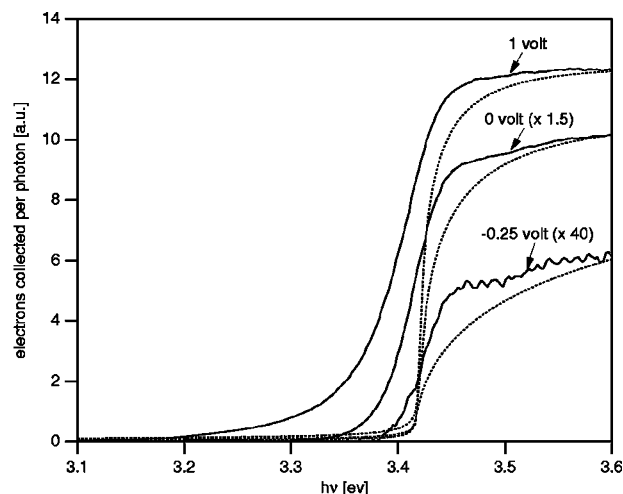

FIG. 4. Photocurrent action spectra of GaN as a function of applied potential (continuous lines). The contributions of direct electron–hole generation obtained from the fits of the PL excitation spectra (Fig. 1) are shown by dashed lines.

constant. At electrode potentials more positive than −0.5 V the intensity decreases, becoming constant at around 0 V. The potential dependence of the excitonic peaks is much weaker than that of the luminescence due to band–band absorption (Fig. 3) which is as expected described by Eq. (1). The difference in luminescence intensity can be explained by an ionization probability P for excitons created inside the depletion layer significantly different from zero and smaller than unity. In this case, the luminescence intensity due to exciton absorption is described by

$$\frac{I_{\mathrm{PL,exc}}}{I_{\mathrm{PL,exc,max}}} = 1 - P(1 - e^{-\alpha W}). \tag{3}$$

The continuous line in Fig. 3 shows a fit to Eq. (3) ($P = 0.6$). The experimental data are well described by this relation, notwithstanding the fact that in this calculation, any electric field dependence of P is neglected. Since the ionization of excitons is expected to lead to electrons and holes in the charge separation layer, a contribution from excitonic absorption is also expected in the photocurrent spectra especially in the subgap region. This contribution is indeed observed in the photocurrent action spectra. Figure 4 shows photocurrent action spectra of the GaN epitaxial layer under the same conditions as the photoluminescence excitation spectra in Fig. 1. A strong contribution to the photocurrent of exciton ionization is observed in the region near and below the band gap. The relative amount of sub and near gap photocurrent strongly increases with the depletion layer width (more positive potentials) consistent with exciton ionization in the depletion layer.

In this letter, we showed that variation of the electrode potential of an n-GaN/solution heterojunction allows for the convenient discrimination between free electron–hole pair generation and exciton creation at room temperature. This result is likely to be general for all semiconductors with an exciton binding energy comparable to kT. The anomalous potential dependence of the intensity of the excitonic luminescence was ascribed to incomplete ionization of excitons in the space charge region.

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