

Yellow luminescence and related deep levels in unintentionally doped GaN films

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The deep level energy distribution associated with the well-known ‘‘yellow luminescence’’ in GaN is studied by means of two complementary deep level techniques: photoluminescence and surface photovoltage spectroscopy. The combined experimental results show that the yellow luminescence is due to capture of conduction band electrons, or electrons from shallow donors (with a maximum depth on the order of the thermal energy) by a deep *acceptor* level with a broad energy distribution, centered at ~ 2.2 eV below the conduction band edge. In addition, the results show that the density of yellow luminescence related states possesses a significant surface component. [S0163-1829(99)16215-5]

In recent years, technological breakthroughs in GaN doping and contacting technologies have resulted in numerous devices, notably the blue-emitting GaN-based laser.¹ Unfortunately, for lack of adequate GaN substrates, GaN films are typically grown on substrates to which they are both lattice and thermally mismatched. Thus, even device grade GaN films possess a high density of grain boundaries, dislocations, and various point defects.² A related consequence in most samples is a large density of electronic gap states. Understanding the nature and the electrical activity of these gap states is therefore of much importance for assessing the degree to which they affect device performance.

Various spectroscopic tools have been employed for studying gap states in GaN, of which photoluminescence (PL) spectroscopy is apparently the most common. A frequent finding is that when GaN films are exposed to super-band-gap illumination, a characteristic yellow luminescence (YL), often intense enough to be observed with the naked eye, is emitted. This luminescence appears as a broad spectral peak, centered around ~ 560 nm (photon energy of ~ 2.2 eV).³ Assuming identical excitation conditions, the ratio of the band-edge and the yellow luminescence peak intensities can be used as an informal figure of merit, indicating the film quality.⁴ The energy position of the gap states involved in producing the YL cannot be directly determined from the PL spectra. To that end, various other spectroscopic tools have recently been used.⁵ However, contradictory models have been proposed^{3,6} and none has become widely accepted. Thus, the nature of the YL related deep levels is still a subject of much debate.

In this paper, we study the YL and its origins in unintentionally doped GaN films by augmenting the common emission-sensing PL measurements with the absorption-sensing surface photovoltage spectroscopy (SPS).^{7,8} The combined results shed light on the energy distribution of the YL-related deep levels and offer some hints as to their spatial position.

The GaN films used in this work were grown using metal-organic vapor phase epitaxy on (0001) oriented sapphire substrates. The growth precursors were ammonia and tri-methyl-gallium. H_2 was used as the carrier gas. The GaN layers were grown at atmospheric pressure and high temperature (1000°C), after a deposition of a thin GaN buffer layer at a lower temperature ($\sim 600^\circ\text{C}$). Samples 1–4 possessed a layer thickness of the order of $4\ \mu\text{m}$ and an effective doping level of $n \sim 4 \times 10^{17}\ \text{cm}^{-3}$. Sample 5 was a thin film of $\sim 2000\ \text{\AA}$, with a doping level of $n \sim 5 \times 10^{18}\ \text{cm}^{-3}$.

Surface photovoltage spectroscopy measurements were conducted inside a dark Faraday cage. The surface photovoltage was measured by monitoring changes in the surface work function. These changes were monitored using the Kelvin probe technique. The latter measures the contact potential difference (CPD), i.e., the difference in work function, between the semiconductor free surface and a vibrating reference probe.^{8,9} A commercial Kelvin probe (Besocke Delta Phi, Germany), with a sensitivity of ~ 1 mV, was used in all measurements. To provide a common ground for the probe and sample, an Ohmic ‘‘back contact’’ of indium was soldered on the periphery of the sample surface, while the Kelvin probe was brought to a distance of about 1 mm from the sample over the free part of the surface. We emphasize that as the ‘‘back contact’’ was not illuminated, the results given below were not influenced by either defects at the metal/GaN interface or the exact resistance characteristics of the contact.⁸

Prior to illumination, each GaN sample was maintained in the dark for an extended period to eliminate persisting effects of previous light exposure. The free surface of the sample was then illuminated using a 250-W tungsten-halogen lamp, or a 150-W xenon lamp, filtered through a 0.25-m grating monochromator. For spectroscopic analysis, wavelengths were scanned from 1200 to 350 nm, in 1-nm steps. At each step, the CPD measurement took place after an illumination ‘‘dwell time’’ in order to approach quasi-steady-state condi-

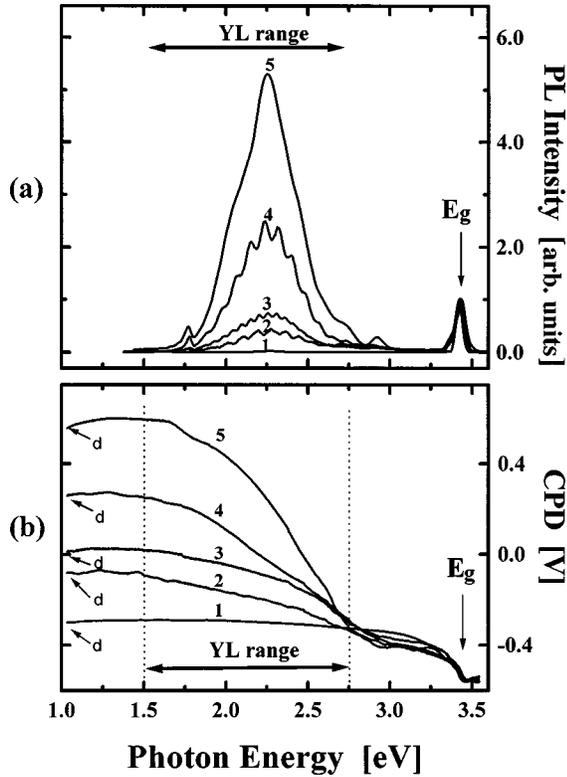


FIG. 1. (a) Photoluminescence spectra of five GaN samples, having different yellow to band-edge luminescence ratios. (b) CPD spectra of the same five samples.

tions. The relaxation time in the dark and the illumination dwell times were established by monitoring CPD transients.

Photoluminescence was excited using a HeCd laser (325 nm, 10 mW). The emitted luminescence was monochromatized, filtered, and sensed using a GaAs photomultiplier tube. Wavelengths were scanned in 1-nm steps from 350 to 890 nm.

Photoluminescence spectra of the five samples are shown in Fig. 1(a). The samples feature various ratios (0.02–5.3) of yellow to band-edge luminescence (YL/BE). The CPD spectra obtained from the same five samples are shown in Fig. 1(b). Both the BE peak and the broad YL peak coincide with CPD changes taking place over the same energy ranges. It is therefore highly likely that the PL and CPD spectra resolve the emission and absorption of photons, respectively, due to electron transitions between the *same* energy levels. Thus, we can concentrate on the CPD spectra for a more elaborate analysis of the deep levels involved.

By definition, the CPD is given by

$$\text{CPD} = (\phi_s - \phi_m)/e, \quad (1)$$

where ϕ_s is the surface work function of the semiconductor, ϕ_m is the work function of the metal, and e is the (absolute value of the) electron charge. Because the metal work function is constant, illumination-induced changes in the CPD are attributed to changes in the semiconductor surface work function. For an n -type semiconductor, the latter may be expressed as

$$\phi_s = (E_c - E_F)_b + \chi_s + e|V_b|, \quad (2)$$

where $(E_c - E_F)_b$ is the energy difference between the conduction band and the Fermi level in the quasineutral region of the sample, χ_s is the surface electron affinity, and $e|V_b|$ is the magnitude of the surface barrier.^{8,9}

A key observation is that the CPD values on the leftmost edge of the curves in Fig. 1(b) (denoted by arrows labeled d) were obtained *in the dark* (with subsequent illumination scanned from low to high photon energies). The dark CPD values of the five samples differ significantly, by as much as ~ 0.9 eV. Figure 1 shows that the higher the YL is, the higher the dark CPD value is. However, at energies exceeding the high-energy edge of the YL peak, the CPD curves of all samples practically merge.

To identify the physical mechanism responsible for the CPD differences and their correlation with the YL, we inspect Eq. (2). The first term, $(E_c - E_F)_b$, does not change appreciably among the different samples. This is because it depends on carrier concentration variations in a logarithmic fashion. The second term, χ_s , is approximately constant. This is because otherwise the CPD curves would not have merged under super-band-gap illumination, but would rather shift uniformly (note that χ_s is illumination insensitive⁸).¹⁰ The merging of the CPD curves under super-bandgap illumination is easily explained, however, by changes in $e|V_b|$. This is because the surface barrier is greatly reduced under such illumination, due to the surface photovoltaic effect. We therefore conclude that changes in the third term, $e|V_b|$, dominate the CPD differences among the samples in the dark. The definite correlation of the surface barrier height to the yellow to band-edge luminescence (YL/BE) ratio indicates that the equilibrium surface barrier increases with increasing density of the YL related gap states.

In principle, the observed gap states can either be spread throughout the *bulk* or be situated at the *surface*. For distinguishing between the two, we consider the dependence of the surface barrier, $e|V_b|$, on the surface and volume charges. By solving the Poisson equation under the depletion approximation, it is easy to show that¹¹

$$e|V_b| = \frac{Q_s^2}{2\epsilon N}, \quad (3)$$

where Q_s is the surface charge density, N is the net donor density in the space charge region, and ϵ is the dielectric constant. For the YL-correlated surface barrier to be dominated by YL related states *in the bulk*, the unintentional doping level N must be dictated by the YL related defects and decrease with increasing YL/BE ratio. In practice, these conditions are not met. No correlation between the YL and the unintentional doping level was found in the present study, nor was such a correlation reported in the literature. Moreover, the YL/BE ratio of sample 5 was actually higher than those of the other samples despite its larger doping. Thus, the dominance of bulk states in the CPD spectra is unequivocally ruled out.

For the YL-correlated surface barrier to be dominated by YL related *surface* states, the surface state density must increase with increasing YL/BE ratio. For the given unintentional doping level of $\sim 10^{17}$ – 10^{18} cm⁻³, Eq. (2) shows that a change in surface state density between $\sim 10^{11}$ – 10^{12} cm⁻² suffices to quantitatively account for the observed change.

These numbers are highly reasonable and are typical for many semiconductor surfaces.⁹ Thus, we positively assign the YL-related gap states, which dominate the surface barrier, to the *semiconductor surface*.

To corroborate the surface assignment of the YL-related states, intensity resolved surface photovoltage experiments were performed (results not shown for brevity). At a photon energy of 2.54 eV, corresponding to excitation of the YL-related deep levels, a superlinear dependence of the surface photovoltage on the illumination intensity was found. This behavior was previously proved to be a “fingerprint” of surface states.¹¹

The dark CPD values indicate a significant depletion layer, i.e., a surface barrier for electrons. We therefore conclude that the involved surface states are *acceptors*. This is because the surface states must be negatively charged in order to produce a surface depletion layer in an *n*-type material. Had the states been donors, they would have produced a weak accumulation layer,⁹ if at all, in disagreement with the experimental data.

Considered in more detail, Fig. 1(b) shows that as the CPD decreases continuously with increasing photon energy over the YL range, the CPD differences between the samples gradually subside and finally all but disappear beyond the YL energy range. We interpret this behavior as follows: the YL-related surface states constitute a broad, distributed state peaked at ~ 2.2 eV, which is mostly filled in equilibrium. Upon illumination, electrons are excited from this broad distribution into the conduction band. This excitation may be direct, but may also proceed through a donor that is shallow enough for thermal excitation to take place. The excited electrons are swept away from the surface under the influence of the surface electric field, the surface charge is reduced, and thus the surface barrier is also reduced [see Eq. (3)]. As the photon energy increases, electrons lying deeper inside the broad gap state distribution can be excited, and the barrier decreases progressively. The common CPD value reached for photon energies exceeding 2.7 eV indicates that the YL contribution to the surface barrier is by and large removed by the illumination and only a relatively small residual surface barrier remains.

Further support for the energy position assignment of the observed states stems from the CPD increase, observed at photon energies of 1 to 1.3 eV, due to the following mechanism. A CPD increase in an *n*-type material must involve minority carrier transitions,^{7,8} which in the present case involve excitation of an electron from the valence band into empty states. Therefore, it is likely that this CPD increase indicates the existence of a deep level, centered ~ 1.2 eV above the valence-band edge. This energy position coincides with that of the YL-related deep level ($E_c - 2.2 \text{ eV} = E_v + 1.2 \text{ eV}$). Thus, the two transitions at ~ 1.2 and ~ 2.2 eV are complementary and involve the same deep level. A sizable CPD response to a majority carrier transition, along with a relatively weak CPD response to the complementary minority carrier transition, is well known in wide-band-gap semiconductors. This is because minority carrier transitions are known to have an inherently weaker manifestation in CPD spectra.^{7,8} We note that the presence of the complementary transition indicates that the YL-related state is not completely filled. This may be due to an incomplete relaxation of

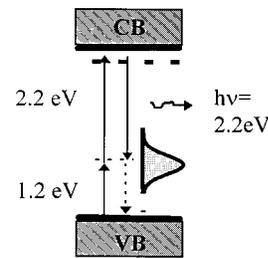


FIG. 2. Schematic energy diagram depicting the YL-related deep levels and transitions.

the YL state, on account of poor communication with the bulk arising from the large surface barrier. Such behavior has been previously reported for other wide-band-gap semiconductors.⁷ A summary of the YL-related deep levels and transitions is schematically shown in Fig. 2.

The emission of YL in GaN films is usually explained by means of two opposing models: the first involves electron transitions either from the conduction band, or from a shallow donor, to a deep state in the lower half of the band gap.^{3,5,12–16} The second involves transitions from a deep state in the upper half of the gap either to the valence band, or to a (relatively) shallow acceptor.^{6,17–20} Our results *strongly support* the first model. Furthermore, in previous studies supporting this first model the acceptor or donor nature of the deep state could not be determined unequivocally.^{12,13,15} For example, Hoffman *et al.* suggested, based on PL, PL excitation, and optically detected magnetic resonance experiments, that the deep level is either a doubly charged donor or an acceptor.¹² The acceptor nature of the state is clearly evident here.

We also note that although all authors reported a broad YL band, detailed studies of the activation energy yielded either 2.2 or 2.5 eV as the dominant energy. We believe that this scatter is because different experiments were sensitive to either the peak of the YL distribution, or its lower-lying edge, respectively. Both energy levels are thus in agreement with our results.

Additional photoconductivity measurements on the same samples,²¹ as well as photoconductivity data reported in the literature^{22,23} also resolve a “yellow absorption” band as in the SPS results. Therefore, the YL-related states are usually analyzed as bulk states. Here, we have shown a distinct surface contribution. One possible explanation is that the YL-related deep levels correspond to, or are enhanced by, grain boundaries, as well as other extended defects, such as dislocations.^{5,24} According to this hypothesis, the surface, being a special case of a grain boundary, would naturally possess a high density of defect states. Further work for testing this hypothesis is underway.

In conclusion, two complementary deep level spectroscopies were used to study YL-related electron transitions. Their combined results show that a broad acceptor state, centered at ~ 2.2 eV below the conduction-band minimum, is related to the YL. Upon illumination with photons ranging from 1.5 to 2.5 eV, electrons are excited from these states to the conduction band, either directly or via a shallow donor. Electron recombination in this state produces the characteristic yellow emission. A broad minority carrier transition,

identified as the complementary of the former, is observed at energies between 1.0 and 1.3 eV. A strong surface band bending, associated with the charged state of the acceptor, indicates a significant concentration of YL-related states at the free sample surface.

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