



Defect formation near GaN surfaces and interfaces

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Abstract

We have used low-energy electron-excited nanoscale-luminescence (LEEN) spectroscopy combined with ultrahigh vacuum (UHV) surface science techniques to probe deep level defect states at GaN free surfaces, metal-GaN contacts and GaN/InGaN quantum well interfaces. Employing energies as low as 100 eV and ranging up to 5 keV, we have been able to establish the local nature of these states and their spatial variation normal to the interface plane on an incremental 10–20 nm scale. Coupled with surface science techniques, these measurements show that a variety of discrete deep levels form deep within the GaN band gap due to (a) native defects, (b) metal-induced bonding, (c) reaction products, and (d), in the case of GaN/InGaN heterostructures, local interface phase changes. These results suggest that deep levels are a common feature at GaN interfaces and hence can play an integral role in charge transfer and the formation of local dipoles at GaN heterostructures. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Deep electronic states are of central importance in determining the bulk emissive and transport properties of GaN. Theoretical calculations and experimental measurements show that the bulk defect and impurity states have energy levels ranging across the band gap [1–4]. While considerable attention has focused on the trapping and recombination properties of such bulk deep levels, relatively little is known about the electronic states at GaN surfaces and interfaces. The presence of localized states at such boundaries can affect Schottky barrier formation and heterojunction band offsets. The nanometer-scale film thicknesses now being used in nu-

merous GaN heterostructures further amplifies the relative importance of such interface electronic features.

In this paper, we present evidence for a variety of discrete electronic states associated with GaN surfaces and interfaces. Such states are possible to identify and distinguish from bulk features with low-energy electron-excited nanoscale-luminescence (LEEN) spectroscopy. We have used the luminescence associated with optical transitions into or out of gap states in order to characterize electronic features near interfaces. This requires the ability to: (a) excite free electron–hole pairs, (b) produce such excitation near “buried” interfaces, and (c) vary this excitation in depth on a nanometer scale. These criteria are met by LEEN spectroscopy, which has already been applied to a wide variety of semiconductor–semiconductor and semiconductor–metal interfaces [5,6].

Considerable research has shown the strong dependence of bulk deep levels in GaN on the specifics of growth and subsequent processing [7,8]. Additional electronic

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states may reside near surfaces and interfaces due to chemical and morphological changes in the crystal. All these extrinsic features can degrade the near band edge (NBE) optical emission as well as transport properties. In this paper, we present evidence for discrete gap states at GaN surfaces, metal-GaN interfaces, and III-V nitride heterojunctions. Furthermore, the use of surface science techniques permits the chemical origin of extrinsic, near-surface states to be investigated.

2. Experiment

The LEEN experiment consists of a low-energy (0.1–5 keV) electron beam impinging on a controlled surface in ultrahigh vacuum (UHV). The minority carriers generated recombine either across the band gap (near band edge (NBE) radiation), through deep levels in the band gap, or via (nonradiative) phonon generation. The depth of excitation can be varied as a function of incident electron beam energy from a few nm to a few hundred nm over this energy range [9]. The incident electron beam produces a cascade of secondary electrons and, subsequently free electron-hole pairs. One can calculate the maximum range of penetration R_B for the Everhart-Hoff relation [10] extending to low energies. The maximum electron-hole pair production of the electron cascade occurs for values approximately one-third of these values. Thus, for example, a 1 keV electron beam produces a cascade of secondaries and generates electron-hole pairs that extend 20 nm below the surface, peaking at ~ 6 –7 nm. Photon emission is collected via IR-UV transmitting optics to photodetectors. This experimental setup is described in previous publications [5,6].

3. Results and discussion

Fig. 1 shows LEEN spectra for GaN grown by molecular beam epitaxy (MBE) under different N deposition conditions. A biased electrode provided a means to deflect ionized N atoms from the plasma source away from the growth surface. Fig. 1 shows dramatically different spectral features for GaN grown with different deflection voltages applied to the electrode. The “yellow” luminescence (YL) that dominates the MBE GaN grown without removing N ions decreases with increasing deflection voltage. Likewise, a shallow defect transition at 3.37 eV decreases as well. A deflection voltage of 700 V can achieve almost two orders of magnitude decrease in these peaks. Furthermore, the electron mobility more than doubles from a value of 300–640 $\text{cm}^2/\text{V s}$ from zero to the highest deflection voltage. These results indicate that the presence of N ions gives rise to yellow luminescence, which in turn corresponds to increased electron trapping

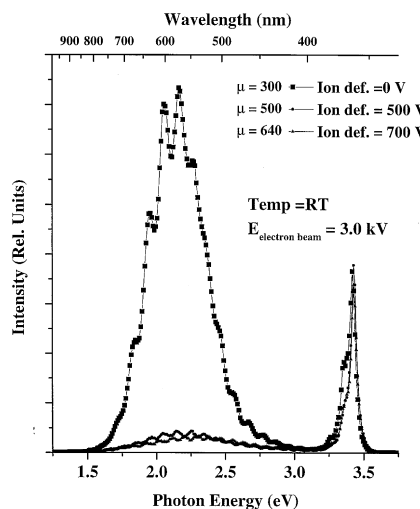


Fig. 1. LEEN spectra with 3.0 keV excitation energy of MBE-grown GaN versus ion deflection voltage. Increasing ion deflection voltage suppresses the midgap and 3.37 eV luminescence.

and reduced mobility. It should also be noted that this yellow luminescence is in fact comprised of at least three overlapping emission peaks centered at 1.75–1.8, 2.15, and 2.4 eV, rather than one broad peak distribution. Similar multiple peak structure in the YL energy range is evident in GaN grown by organometallic chemical vapor deposition (OMCVD) [4]. Finally, it should be noted that the emission spectra in Fig. 1 correspond to a total range of excitation R_B of 90 nm – well below the free surface. Depth-dependent spectra (not shown) reveal that the yellow luminescence is relatively constant versus depth for the GaN grown without deflection. On the contrary, the GaN grown with N ions deflected shows YL increases by over an order of magnitude for near-surface excitation (≤ 1 keV corresponding to $R_B \leq 20$ nm). This increased emission suggests either defects formed preferentially near the free GaN surface or the influence of residual N ions associated with the termination of growth.

Fig. 2 illustrates a Ga-related defect at the surface of a GaN specimen grown by metallorganic MBE (MOMBE). The as-grown specimen shows YL with intensity completely dominating the NBE peak for all penetration depths. After annealing at $T > 1250^\circ\text{C}$, dramatic new features appear, including a sharp (< 0.025 eV FWHM) peak at 1.81 eV and a broad (0.33 eV FWHM) peak centered at 1.66 eV. Similar emissions have been reported previously as “red luminescence” that appeared when excited via a broad C-excitation band [10]. Auger electron spectroscopy (AES) measurements of surface composition establish a $> 10\%$ decrease in the Ga/N ratio and a residual C and O concentration of 6% C and $< 10\%$ O. Depth-dependent spectra reveal that the

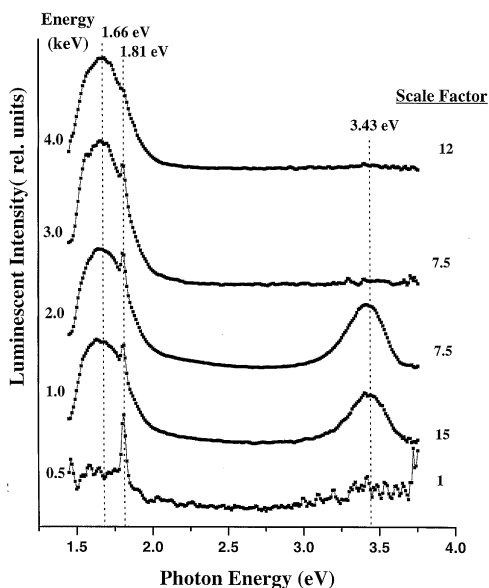


Fig. 2. LEEN spectra as a function of excitation energy and depth showing the near-surface features between 1.5 and 2.0 eV induced by 1250°C annealing.

1.81 eV peak intensity decreases with deeper excitation. The sharpness of this feature, its near-surface location, and the decrease in relative Ga concentration together suggest emission either from a Ga-related nanostructure, e.g., Ga droplets, or a surface segregated impurity, e.g., Al or Cr. The broader feature corresponding to the Ga-deficient surface is at least 120 nm thick. The “bulk” nature of this emission suggests the formation of a defect complex associated with a Ga deficiency. Interestingly, this layer forms under high-temperature conditions usually associated with preferential N desorption. The YL emission does not appear to increase under these conditions. Subsequent UHV deposition of a 1 nm Ga overlayer on this heat-treated surface reduces (but does not eliminate) the 1.66 eV peak and, to a lesser extent, the YL shoulder within the top 6–20 nm, further confirming the Ga-deficient nature of the lower energy feature. The contrast in behavior between these red luminescence features versus the YL indicates that different defects can become dominant recombination sites with different surface treatments near the free GaN surface.

Defect formation also occurs at metal–GaN interfaces. Fig. 3 illustrates LEEN spectra taken at different depths below a bare, MBE-grown GaN surface versus that of a similar crystal coated with 30 monolayers (4.8 nm) of Mg [6]. This metal–GaN interface was formed by evaporation in UHV on a LEED-ordered, MBE-grown surface, then annealed at 1000°C [11]. Fig. 3 shows broad, nearly featureless emission extending from ~ 3 to below 1.4 eV and relatively uniform at all depths. In contrast

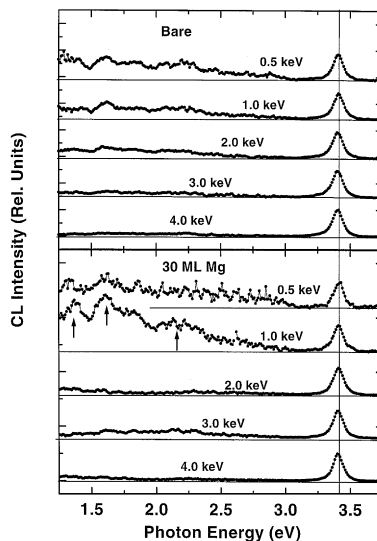


Fig. 3. LEEN spectra as a function of excitation energy and depth for a bare and a Mg-covered GaN single crystal showing the new emissions induced by the metal overlayer plus high-temperature anneal.

the Mg-covered GaN shows a maximum in sub-gap emission at excitation depths of 3–6 nm. Despite the low signal intensities, this emission indicates peak features at 1.4, 1.6, and 2.15 eV. Soft X-ray photoemission spectroscopy (SXPS) measurement of the Fermi level movement for this same sample show that it stabilizes at 2.2 eV above the valence band (1.2 eV below the valence band) [12]. Interestingly, other metals on UHV-prepared n-type GaN surfaces are known to stabilize the Fermi level within a range of 2.0–2.6 eV [13]. This suggests that metal-induced states at the Mg–GaN interface play an active role in the Schottky barrier formation. However, the role of defects may not extend to all metal contacts with GaN. For example, Al–GaN interfaces annealed at 1000°C in UHV result in a reacted interface layer rather than new defect formation [6].

New localized states are also present at GaN heterojunctions. We obtained LEEN depth-dependent spectra from an InGaN quantum well “buried” 30 nm below the free GaN surface. These quantum well structures consisted of an $\text{In}_x\text{Ga}_{1-x}\text{N}$ layer ($x = 0.14$ or 0.28) with an average thickness of 2 nm. This layer was confined between a $2\text{ }\mu\text{m}$ thick Si-doped ($n = 3 \times 10^{18}\text{ cm}^{-3}$) GaN layer grown at 1050°C over a (0 0 0 1) sapphire substrate and a 30 nm GaN capping layer not intentionally doped and grown at roughly 800°C, the same growth temperature as the $\text{In}_x\text{Ga}_{1-x}\text{N}$ layer [14]. The bowing parameter calculations of In concentration due to McCluskey et al. [15] yield x values approximately one half of those extracted from a linear extrapolation between the GaN

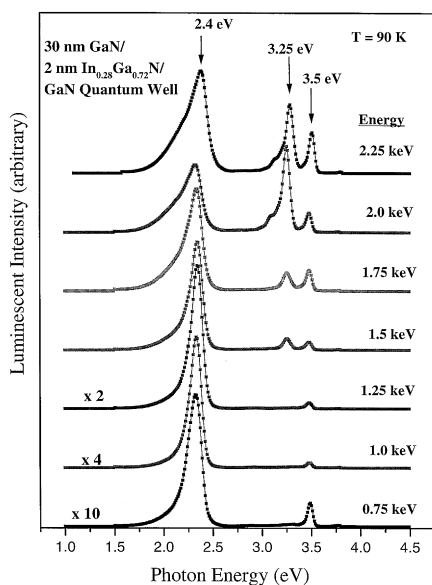


Fig. 4. LEEN spectra versus incident beam energy and depth for a relatively In-rich InGaN quantum well confined buried 30 nm below the GaN surface. At energies corresponding to depths just beyond the quantum well, new emission appears at 3.25 eV, corresponding to a localized electronic state at the deeper of the InGaN–GaN interfaces.

and InN band gaps (Vegard's Law) [14]. Fig. 4 illustrates for beam energies below 1 keV, showing quantum well emission at 2.4 eV that increases relative to the GaN NBE peak. This relative increase corresponds to an increasing penetration of the electron beam and an increase in minority carriers reaching the quantum well region. The quantum well versus NBE ratio reaches a maximum at 1 keV and corresponds to excitation of free electron–hole pairs peaking at depths of ~ 6 –7 nm and ranging down to ~ 20 nm, followed by hole diffusion to the quantum well with a diffusion length $L_D < 25$ –28 nm. The latter was extracted from a fit to the onset of quantum well emission in a $x = 0.14$ $\text{In}_x\text{Ga}_{1-x}\text{N}$ layer that exhibited a similar ratio maximum at 750 eV [16].

In addition to the quantum well and NBE emissions, a new emission feature appears at 3.25 eV at excitation voltages above 1.25 eV. The intensity of this feature rises rapidly with increasing voltage, reaching a maximum relative to both the quantum well and NBE emissions at 2.0 keV. With further voltage increases, LEEN spectra show a decrease and disappearance of this 3.25 eV feature. The appearance of this feature at energies corresponding to the quantum well indicates that its location lies close to that of the quantum well. On the other hand, the 3.25 and 2.7 eV features have different depth dependences, indicating that the former is not a quantum well emission per se, but rather emission from a region localiz-

ed near the quantum well. That it reaches a maximum relative intensity at voltages above the voltage at which the quantum well is maximum suggests that this localization is at or near the deeper quantum well interface. The line shape of the 3.25 eV peak is relatively unchanged with increasing energy. Researchers have found a nearly identical peak feature at 3.26 eV due to the NBE of cubic GaN [5]. Even the lower energy side bands in the LEEN spectra agree with the phonon replicas identified with the cubic phase emission. The formation of cubic GaN in a thin, interfacial region at the deeper quantum well interface is not unexpected, given the low temperature used to begin the InGaN growth and the relatively high In concentration, both of which could induce stacking faults, known to promote nucleation of cubic phase growth [17]. A new quantum well emission is a less likely explanation for this localized feature, given the difference in depth dependence of the quantum well versus 3.25 eV emission intensities. Phase segregation is also a less plausible explanation, given the lack of an even more In-rich peak emission at lower energies lower than 2.4 eV but above the InN band gap (e.g., 1.8 eV) [18]. Finally, transmission electron microscopy (TEM) images of the higher versus lower In concentration quantum well showed more complex lattice structure near the interface. Thus, the most likely origin for the “buried” interface feature is emission from a nanometer – scale layer of cubic GaN near the InGaN/GaN buffer layer interface due to the change in growth temperature and composition.

4. Discussion

The results presented above demonstrate that several types of localized electronic states can occur at GaN surfaces and interfaces. The deep level energies of these states appear at a wide range of energies across the GaN band gap. Incorporation of N ions in an MBE-grown film is shown to induce “yellow” luminescence features at multiple energies and with intensities that increase toward the free surface. The dependence of this intensity on the extent of ionized N incorporation suggests that point defects alone are not sufficient to account for YL emission. Other extrinsic parameters such as H incorporation may be required to account for the ion-dependent results. High-temperature annealing yields Ga-deficient surfaces and new features distinct from the YL emission. The correspondence of this luminescence with features associated with C doping suggests that changes in the near-surface C impurity bonding can alter the electrical activity of surface trap states. C redistribution in GaN is not expected even for higher temperatures (i.e., 1450°C) [19]. The lack of any increase in YL luminescence with a decrease in near-surface Ga suggests that more than Ga vacancies [1,2] are needed to account for this common defect feature. Mg–GaN Schottky barriers induce a set of

“buried” interface features localized at the intimate contact on a nanoscale with energies at and below that of “yellow” luminescence. The correspondence of the defect energies with the range of UHV Fermi level stabilization energies suggests that defects induced by GaN metallization play a significant role in Schottky barrier formation. Finally, we have observed localized states of an entirely different nature at heterojunction interfaces between GaN and InGaN. LEEN spectroscopy clearly highlights the localized nature of these states and provides strong evidence for cubic phase formation on a nanometer scale. The emission from such a cubic “interphase” is quite close to the band offset calculated for a “quantum-like region of zinc-blende material” surrounded by wurtzite GaN [20]. The change in electronic structure at all these “buried” GaN interfaces and free surfaces has until now not been available. Despite the highly localized nature of these states, it is possible to associate their energies with those of defects reported for bulk GaN. The results provided in this paper show that a complete understanding of surface recombination, charge transport across Schottky barriers, and heterojunction barrier confinement involving GaN surfaces and interfaces requires a determination of the extrinsic electronic states present at these junctions.

5. Conclusions

Low-energy electron-excited nanoscale-luminescence spectra demonstrate the ability to detect new electronic structure at GaN surfaces and interfaces. These results provide evidence for discrete native defect states across the band gap. Furthermore, both the free surface and heterointerface states display a strong dependence on growth techniques and specific chemical interactions. By feeding back to the growth process, this characterization provides a new approach to monitor and minimize localized deep levels at Schottky barriers and heterojunctions.

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