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Repository Citation

Goss, S. H., Sun, X. L., Young, A. P., Brillson, L. J., Look, D. C., & Molnar, R. J. (2001).

Microcathodoluminescence of Impurity Doping at Gallium Nitride/Sapphire Interfaces. *Applied Physics Letters*, 78 (23), 3630-3632.

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Microcathodoluminescence of impurity doping at gallium nitride/sapphire interfaces

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(Received 21 February 2001; accepted for publication 17 April 2001)

We have used low-temperature cathodoluminescence spectroscopy (CLS) to probe the spatial distribution and energies of electronic defects near GaN/Al₂O₃ interfaces grown by hydride vapor phase epitaxy (HVPE). Cross sectional secondary electron microscopy CLS shows systematic variations in impurity/defect emissions over a wide range of HVPE GaN/Sapphire electronic properties. These data, along with electrochemical capacitance–voltage profiling and secondary ion mass spectrometry, provide a consistent picture of near-interface doping by O diffusion from Al₂O₃ into GaN, over a range 100–1000 nm. © 2001 American Institute of Physics. [DOI: 10.1063/1.1377858]

The nature of atomic bonding and local electronic structure at GaN heterojunction interfaces has assumed increased significance as crystal quality improves and advanced wide-gap semiconductor devices scale down to the nanometer regime. GaN diffusion, interface reactions, and defect formation are of critical importance in controlling carrier transport through the epitaxial thin films. In particular, near the GaN interface with sapphire, the most common growth substrate for device development, degenerate doping, and high conductance^{1,2} degrade the control of the transport in the overall epilayer. The physical origin of the donors may involve: (i) native defects, impurities, or complexes generated from the substrate^{3–5} or the initial growth surface; or (ii) morphological defects such as dislocations or stacking faults. In order to determine the physical nature of these donors, we used low temperature (10 K) electron-excited luminescence spectroscopy in an ultrahigh vacuum (UHV) scanning electron microscope (SEM) to measure defect emissions from GaN/Al₂O₃ junctions with sheet carrier densities that varied over two orders of magnitude. We carried out cross sectional cathodoluminescence spectroscopy (CLS) of these interfaces and compared these results with near-interface free-carrier profiles from electrochemical capacitance–voltage (ECV) measurements and sheet free-carrier concentrations n_{int} measured by the Hall effect. Besides the expected line broadening in the near-interface region, CLS reveals a feature about 26 meV below the usual shallow donor-bound exciton D^0X line. We interpret this as a ground–state D^0X transition deeper than that of the shallow bulk donor, whose spectral intensity versus spatial distribution correlates with the O dif-

fusion into GaN measured by secondary ion mass spectroscopy (SIMS) and its variation with ECV-measured doping density.

The GaN/Al₂O₃ layers were grown by chloride-transport hydride vapor phase epitaxy (HVPE) from several sources, designated A, B, and C. Source A material incorporated a ZnO buffer layer prior to GaN growth, but the others did not. A modified JEOL 7800F SEM Auger microprobe (base pressure 8×10^{-11} Torr) fitted with an Oxford Scientific Mono CL monochromator, a liquid He cold stage, and a visible-UV sensitive photomultiplier tube provided CL spectra. We produced cross sections by scoring the sapphire and cleaving between glass cover slips. CL spectra were obtained using 5 keV electron beam energy (total penetration depth ~ 160 nm parallel to the interface) and 1 nA current over a $0.5 \times 0.5 \mu\text{m}^2$ raster square area.

The inset to Fig. 1 displays a typical room temperature log CL spectrum for a HVPE GaN/Al₂O₃ interface (specimen A1) with $n_{\text{int}} = 8 \times 10^{14} \text{ e/cm}^2$, showing peak features at 3.8, 3.42, 2.9, and 2.2 eV. (Note that the 1.7 and 1.9 eV lines are just second-order transitions.) The 3.42 and 2.2 eV features correspond to well-known emissions of the GaN near band edge (NBE) and yellow luminescence (YL), respectively. The NBE, YL, 3.8, and 2.95 eV (“blue”) peaks exhibit Gaussian line shapes in linear spectra at the energies shown. Their relative peak intensities appear for a similar specimen (A2, $n_{\text{int}} = 5.9 \times 10^{14} \text{ e/cm}^2$) as a function of raster center distance d_{int} from the interface in Fig. 1. The GaN NBE emission increases rapidly within the first 10 μm from the interface into the GaN bulk, then gradually over the next 60 μm . The YL emission shows a more gradual increase with d_{int} over the same depth range. Significantly, the absolute YL intensity and its value normalized to the GaN NBE intensity both increase while dislocation density decreases with increasing $d_{\text{int}} > 10 \mu\text{m}$. This result suggests that dislocations are not the source of YL in the “bulk” region.⁶ The low YL

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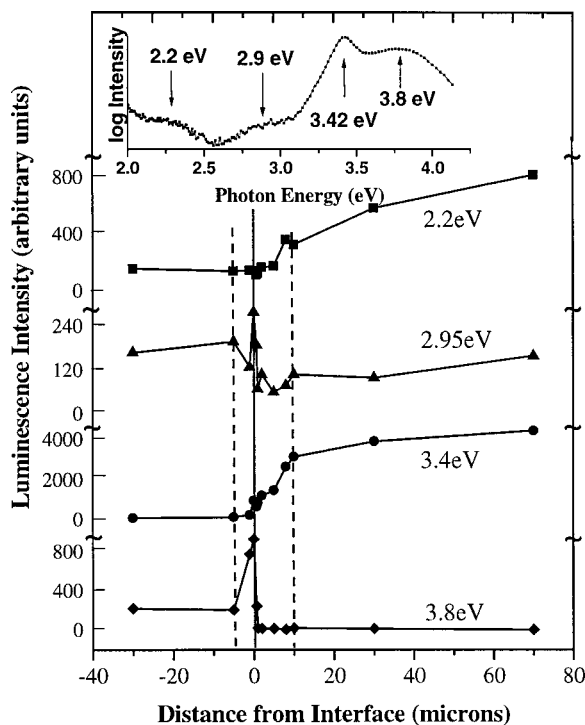


FIG. 1. CL intensities vs d_{int} of peak features at 3.42 (GaN NBE), 2.2 (YL), 2.9 (blue), and 3.8 eV and (panel) a representative CL spectrum of the HVPE GaN/Al₂O₃ interface.

intensity for $d_{\text{int}} < 2 \mu\text{m}$ may be due to competing recombination pathways, e.g., via impurity levels. Cr emission at 1.78 eV (not shown) from the Al₂O₃ decreases rapidly within this $d_{\text{int}} < 10 \mu\text{m}$. The 3.8 eV peak has low intensity within the Al₂O₃, increases with interface proximity, then disappears in the GaN. It can be due to Al–N–O complexes, since 3.8 eV emission in AlN has been assigned to O impurities,⁷ and nitridation of Al₂O₃ forms an amorphous AlN_xO_{1-x} layer.⁸ The broad 2.9 eV blue emission intensity is negligible within the Al₂O₃ or the bulk GaN but is observed for $d_{\text{int}} < 0.2 \mu\text{m}$. Unlike the 2.9 eV emission commonly reported for heavily Mg-doped *p*-type GaN, ours is in a *n*-type sample. Pankove *et al.*⁹ have reported broad 2.9 eV CL emission for Zn-doped GaN. Interfacial Zn might be plausible since Source A employed a ZnO buffer on the Al₂O₃. Such a treatment can result in a Zn-spinel structure¹⁰ and residual Zn impurities near the interface. However, the ZnO was thermally desorbed prior to growth, and in any case, sources B and C did not use such a treatment.

In order to further elucidate the near-interface donor, we have carried out low temperature (10 K) CLS as a function of d_{int} . The CL spectra in Fig. 2 (specimen B, $n_{\text{int}} = 5.0 \times 10^{15} \text{e/cm}^2$) exhibit typical sharp features in GaN, i.e., shallow-donor-bound exciton (D^0X) transitions at 3.473 eV and donor-acceptor-pair (DAP) transitions at 3.2–3.3 eV, followed by a sequence of longitudinal optical phonon replicas ($\Delta h\nu = 92\text{--}93 \text{meV}$). The dominant acceptor may either be C,¹¹ detected by SIMS in similar samples,^{12,13} or the Ga vacancy, detected by positron annihilation.¹³ However, it is not likely Mg, which was not detected by SIMS.¹³ These features are common to GaN at all depths. At $d_{\text{int}} \leq 1 \mu\text{m}$, an additional feature appears at 3.447 eV, somewhat broader than the 3.473 eV peak. A broad structure is not unexpected in

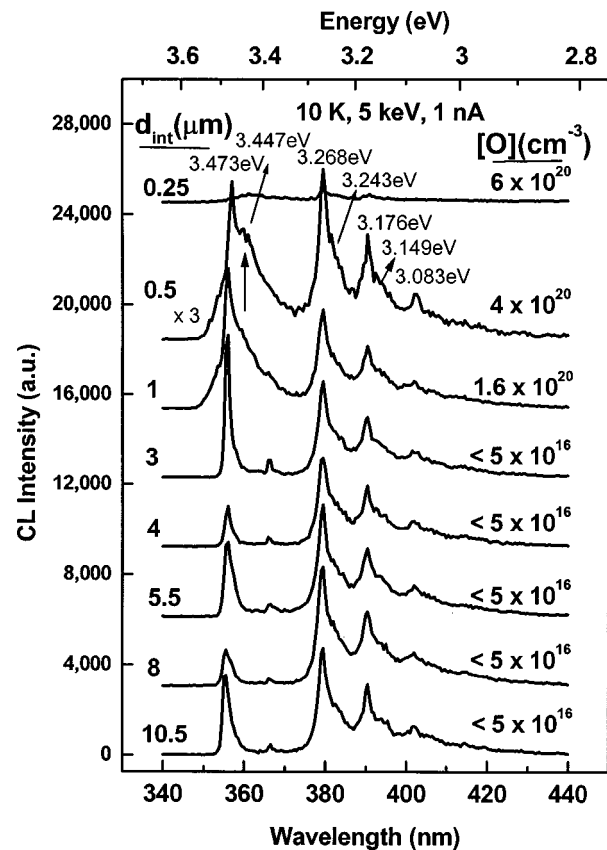


FIG. 2. Low temperature CL spectra of sample B showing added 3.447 eV shoulder features near the interface.

this highly degenerate region, due to band tailing and band filling (Moss–Burstein) effects. The appearance of both sharp and broad features may be due to inhomogeneity parallel to the interface plane reported previously in similar material.¹⁴ Thus, the 3.447 eV line may represent high-concentration regions which are downshifted from the 3.473 eV peak because of band tailing. The 3.449 eV peak may also be a two-electron replica of the 3.473 eV line,¹⁵ because such a line would be expected at $3.473 \text{eV} - (3/4)E_D$, where E_D should be about 34 meV. That is, the final state of the 3.473 eV transition is the ground state ($n=1$) of the donor, whereas the 3.447 eV transition would then have an $n=2$ final state. But if this latter model were correct, then the two transitions might be expected to have about the same line width, which is not the case. The only donor with a high enough concentration to give the observed line broadening of the 3.447 eV line is O, because O increases strongly near the interface, whereas the other major candidate, Si, does not.¹³ SIMS [O] concentrations characteristic of the [O] diffusion appear in Fig. 2. No other donor impurity is localized in this depth range. Hence, the intensity versus depth distribution indicates that O impurities diffused from the Al₂O₃ are the origin of the high sheet carrier concentration.

Another possibility for the 3.447 eV transition is an exciton bound to a deep donor or acceptor. If the Haynes factor is 0.1–0.2, then this deep center would have an energy of about 150–300 meV from a band edge. An acceptor-bound exciton would be the most likely candidate, since acceptor centers are clearly evident from the strong DAP transitions. Of all possible acceptors, only the Ga vacancy would have a high enough concentration to produce such a broad line.

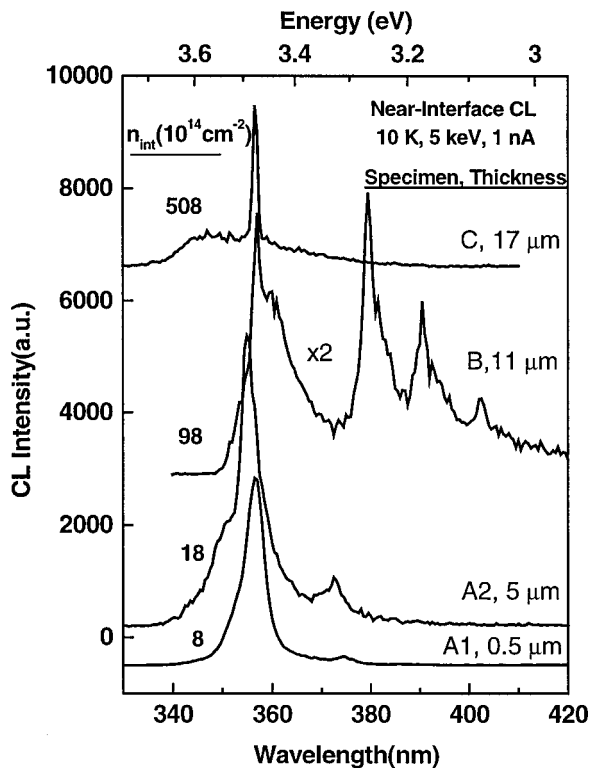


FIG. 3. HVPE GaN/Al₂O₃ CL near-interface spectra. Band tailing, band filling, and possible alloying, are evident at higher sheet carrier concentration.

However, the YL emission typically associated with Ga vacancies is measured to be low in this region, again supporting the association of the 3.447 eV transition with high concentrations of the O donor.

Figure 3 provides a comparison of 10 K NBE spectra from HVPE GaN/Al₂O₃ interfaces with different n_{int} . Line broadening is evident in all cases, as expected. However, sources B and C appear to have sharp lines on top of broad lines, as just discussed. We believe this is due to more inhomogeneity in these layers, as borne out by the SIMS and other CL data. For sample C, a broad feature centered at 3.59 eV appears. Unlike the case for impurity band filling, even for impurity concentrations $> 10^{20} \text{ cm}^{-3}$,¹⁴ this peak is centered well above the conduction band edge and may be due in part to GaN–Al alloying. Such Al_xGa_{1-x}N alloying and NBE features are observed at Al–GaN interfaces,¹⁶ and Al–N bonding is not unexpected, given the O release from Al₂O₃ at the atomic-scale interface. Pregrowth nitridation of sapphire for such specimens¹⁷ should further enhance Al–N bonding and alloying.

In conclusion, we observe both sharp and broad NBE CL

lines near the interfaces of HVPE GaN layers grown on sapphire, evidently due to lateral inhomogeneity in the interface regions. The sharp lines are donor-bound excitons, strongly associated with O shallow donors in the relatively good material, while the broad lines may either be donor-bound excitons in the more highly-concentrated material, or acceptor-bound excitons associated with the Ga vacancy. In either case, these spatial correlations between electronic and chemical impurity distributions confirm the high concentrations of diffusion-induced dopants at the GaN/Al₂O₃ interface.

This work is supported by the Office of Naval Research, the National Science Foundation, the Air Force Office of Scientific Research, and the Department of Energy (depth-dependent measurements). The authors thank Drs. T. Paskova (Linköping University) and R. Vaudo (ATMI) for samples, as well as Drs. S. Mitha and S. Novak (Chas. Evans Associates) for SIMS profiles. The Lincoln Laboratory portion of this work was sponsored by the Office of Naval Research under Air Force Contract No. F19628-00-C-0002. Opinions, interpretations, conclusions, and recommendations are those of the authors and not necessarily endorsed by the United States Air Force.

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