

Formation mechanism of a degenerate thin layer at the interface of a GaN/sapphire system

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It has recently been suggested that the thin degenerate layer found at the GaN/sapphire interface results from a high concentration of stacking faults. The studies of this letter, however, show that this is not the most likely explanation for the presence of such a degenerate layer. Using x-ray energy-dispersive spectroscopy and secondary ion-mass spectroscopy, profile distributions of elements Ga, N, O, C, and Al, near the interface, have been obtained. The distributions reveal very high O and Al concentrations in the GaN film within 0.2 μm from the interface, together with a material depletion of Ga and N. Such conditions strongly favor n^+ conductivity in this interfacial region because not only are N-vacancy and N-site O donors present, but Al incorporated on the Ga sublattice reduces the concentration of compensating Ga-vacancy acceptors. The two-layer (film plus interface) conduction has been modeled, and the effect of conduction in the GaN film thus isolated. © 2000 American Institute of Physics. [S0003-6951(00)00302-8]

Most of the GaN (also InGaN and AlGaN) material used so far for device development consists of epitaxial growth on sapphire. Because of the large lattice mismatch (14%) between GaN and sapphire, a thin, highly dislocated region is generated at the layer/substrate interface to relieve the strain, and the structural properties of this interface region have been studied in great detail.¹ However, little is known at present about the electrical and optical properties of the interface.

Gotz *et al.*² have progressively thinned a 13- μm -thick HVPE layer down to 1.2 μm , and their results have suggested that a significant high donor concentration must exist near the interface. By performing Hall measurements, as the layer thickness in their sample was reduced from 13 to 1.2 μm , these authors using a two-layer model³ estimated that the sheet concentration of donors in the interfacial region exceeded 10^{15} cm^{-2} . Capacitance-voltage measurements, on the other hand, showed that $N_D - N_A$ for the 13- μm -thick bulk film was relatively constant at about $5 \times 10^{16} \text{ cm}^{-3}$, equally with a much lower sheet concentration of only about $7 \times 10^{13} \text{ cm}^{-2}$. The conclusion was, therefore, that the Hall measurements were being strongly affected by an interfacial region.

In this letter, the formation mechanism of the interfacial n^+ layer will be discussed; a subject not yet considered in

the published literature. The discussion focuses on profile distributions of elements Ga, N, O, Al, etc., near the interfacial region as obtained by x-ray energy-dispersive spectroscopy (XEDS) and secondary ion-mass spectroscopy (SIMS). These data suggest extremely high concentrations of Ga and N vacancies close to the interface in the GaN film. It is argued that the N-vacancy together with N-site O form dominant donors and sources of electrons. It is further argued that while the Ga vacancy would tend to compensate the donors, the compensation ratio could be greatly reduced with Al diffusing from the sapphire, incorporating at the Ga sites. Finally, the method used previously⁴ for fitting both mobility and carrier concentration data will be presented but within the framework of the two-layer model. The agreement with experimental data is shown to be excellent.

The samples used in the present work were grown by the two-flow MOCVD method, which has been described in a previous work.⁵ In particular, a 300 Å GaN buffer layer was grown between the GaN film and the sapphire substrate of (0001) orientation. Prior to growing the buffer layer, the substrate was hydrogenated at 1050 °C. The thickness of the GaN film was 2.0 μm . The Hall measurements are the same as those in Ref. 4. The XEDS measurements were carried out by a scanning electron microbeam (SEM) (Cambridge Co.). An electron beam of 100 Å diam was scanned across the sample's lateral cross section in order to find the atomic concentrations across the interface. The appropriate ZAF [atomic number (Z), absorption (A), and fluorescence (F)] correction factors were made to the XEDS data to obtain the correct atomic concentrations.⁵

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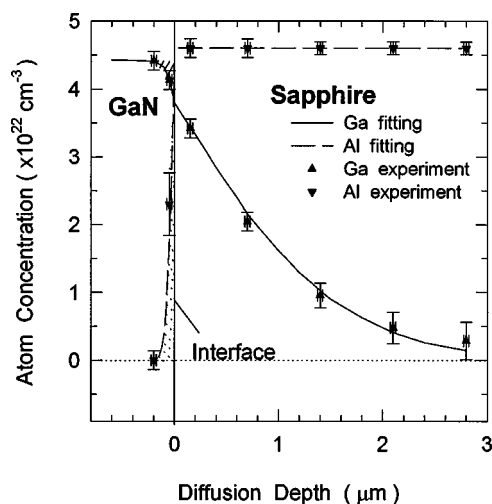


FIG. 1. Concentration distributions of Ga and Al as a function of depth obtained from XEDS. The Ga diffusion into sapphire and Al diffusion into GaN are fitted by complementary error functions. The Ga vacancies and the back-diffused Al are expressed by the oblique real lines and the oblique dashed lines, respectively.

Figure 1 shows the detail of the Ga and Al atomic profiles as obtained from XEDS spectra near the interface of the GaN-sapphire system, where $x < 0$, $x = 0$, and $x > 0$ correspond to the GaN film, the interface, and the sapphire substrate, respectively. The absolute concentration scales of Fig. 1 are obtained assuming a negligible concentration of vacancies in the film and substrate, an Al concentration of $4.6 \times 10^{22} \text{ cm}^{-3}$ in the sapphire (Al_2O_3), and a Ga concentration of $4.5 \times 10^{22} \text{ cm}^{-3}$ in the GaN film. As in our previous work,⁵ a large amount of Ga diffusion into the sapphire is seen to have occurred with a falloff distance $\sim 1 \mu\text{m}$. It is also seen that the Ga concentration decreases from its bulk value of $4.5 \times 10^{22} \text{ cm}^{-3}$ at $x = -0.2 \mu\text{m}$ to $3.7 \times 10^{22} \text{ cm}^{-3}$ at $x = 0$, indicating an appreciable Ga deficiency in this range. This deficiency on its own would not account for the quantity of Ga in the sapphire and it appears that Ga is diffusing out of the bulk film. The large Ga concentration gradient on the film side of the interface confirms this view. In the ideal case of the Ga deficiency being in the form of V_{Ga} we obtain $[V_{\text{Ga}}] = 2.2 \times 10^{21} \text{ cm}^{-3}$, and for the average concentration of Al in the interface region a value of $1.4 \times 10^{22} \text{ cm}^{-3}$ which is over six times greater than $[V_{\text{Ga}}]$. This concentration ratio suggests that the Ga vacancies [often taken to be the main source of acceptors in undoped GaN (Ref. 6)] could be totally replaced by the diffused Al, even though only one sixth of the Al can substitute for the same group-III Ga atoms. It is noted that for the epitaxy methods, such as MOCVD and HVPE, rather high temperatures (higher than 800°C) are required for growth. At such sustained elevated temperatures ($T = 1050^\circ\text{C}$ for MOCVD), atomic diffusion would appear to be a dominant process associated with the film's growth allowing Al atoms to diffuse to and fill the Ga sites in the near-interface region in the film.

In order to obtain a more detailed picture of the defects or impurities present in the *n*-GaN film, we investigated a depth profile of five elements (Ga, N, O, Al, and C) using SIMS. As shown in Fig. 2, the intensities of the five elements are only relative because of their different SIMS yields. However, we can obtain absolute concentration distribution

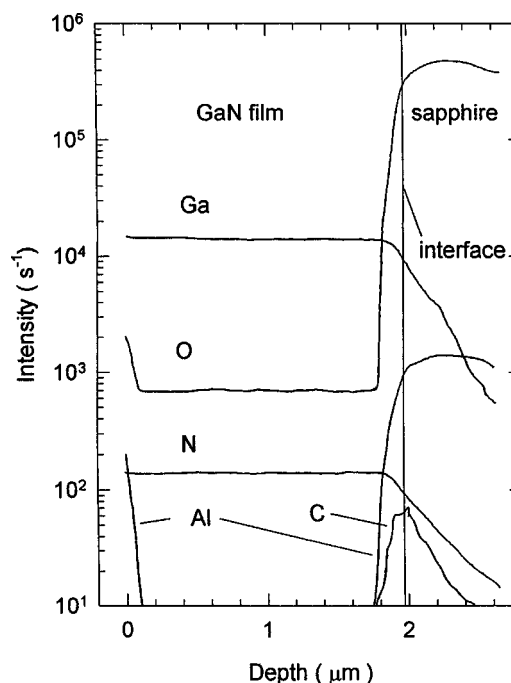


FIG. 2. SIMS depth profile of an *n*-GaN film on a sapphire substrate. The intensities of the five elements are only relative because of their different yields in SIMS. The high intensities of O and Al near the surface are due to a segregation effect.

of Ga, N, Al, and O based on the following approximations:

(i) The concentrations of Ga vacancies and N vacancies (V_{Ga} and V_{N}) in the GaN film, which are at some distance from the interface region ($\sim 0.2 \mu\text{m}$, from the SIMS spectra), are not high (i.e., they are less than 10^{22} cm^{-3}). Based on this reasonable assumption, the concentration of Ga (or N) in the film is $4.5 \times 10^{22} \text{ cm}^{-3}$.

(ii) The diffusing source of Al and O is from the sapphire substrate. This is due to the fact that the diffusion is associated with the film growth process.⁵ Absolute concentrations of Al and O in the film may, therefore, be obtained by referencing to the known values in the sapphire, namely, 4.6×10^{22} and $6.9 \times 10^{22} \text{ cm}^{-3}$, respectively.

Based on these assumptions, the calculated average concentrations of V_{Ga} , V_{N} , O, and Al in the interface region are $5 \times 10^{21} \text{ cm}^{-3}$, $5 \times 10^{21} \text{ cm}^{-3}$, $2.4 \times 10^{22} \text{ cm}^{-3}$, and $3.5 \times 10^{22} \text{ cm}^{-3}$, respectively. As with the XEDS data, these concentrations lead to an expectation that most Ga vacancy sites are replaced by the group-III element Al at the interface. This follows not only from the copious amount of Al present at the interface, but also from the fact that Al has similar chemistry to Ga. Since the Ga vacancy is believed to be a dominant acceptor in GaN, it then follows that the compensation ratio of the interface layer would be greatly reduced.

Turning now to donor sites, we see an opposite tendency. If the main source of the donor is from the N vacancy⁷ or from the N-site oxygen,⁸ the donor concentration could be extremely high in the interface layer with donor sites present at the 10^{21} – 10^{22} cm^{-3} level and with the aforementioned reduction in V_{Ga} acceptor sites, an extremely high ($\sim 10^{21} \text{ cm}^{-3}$) electron density would be expected. Clearly, this electron concentration would be degenerate and temperature independent, since the Mott concentration in

GaN is about $1 \times 10^{18} \text{ cm}^{-3}$,⁹ and the concentration at which the Fermi level enters the conduction band is about $6 \times 10^{18} \text{ cm}^{-3}$.¹⁰

The above arguments explain why, on the basis of atomic interdiffusion during growth, a thin n^+ interface layer forms between the sapphire and the GaN film. The XEDS and SIMS data both suggest the thickness of this layer to be about $0.2 \mu\text{m}$. It is with this thin degenerate layer in mind that attention is now turned to modeling its effect on Hall measurement data.

The temperature-independent mobility μ_2 and concentration n_2 (from the interface layer properties) allow an easy separation of the bulk-film Hall properties, μ_{H1} and n_{H1} , from the measured two-layer properties, μ_H and n_H .³ Using this two layer model, our Hall data give an interfacial carrier density $n_{H2} = 2.2 \times 10^{20} \text{ cm}^{-3}$, which is lower than that obtained from the XEDS and SIMS results of $\sim 10^{21} \text{ cm}^{-3}$. The most likely explanation is that the GaN of the interface layer is not of perfect crystal structure. The lattice mismatch and different thermal conductivity between the GaN film and sapphire is so large that a "quasicrystalline" layer results.¹ The carrier concentration is lower than that of V_N and N-site oxygen partly because, in such an imperfect layer, only some of the latter are electrically active and partly because the dislocations present would trap carriers. From Eqs. (1) and (2), the extracted film concentration n_{H1} and mobility μ_{H1} of a typical sample are plotted in Figs. 3(a) and 3(b), respectively.

To fit the carrier concentration data, we use a two-donor model.⁴ Based on photoluminescence (PL) measurements,^{11,12} the second is a deeper shallow donor with $E_C - E_2 = 42 \text{ meV}$. Figure 3(b) shows the corrected room temperature μ_{H1} to be $430 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in good agreement with the compensation ratio $C = 0.6$ (Ref. 13) (for the calculated results of the carrier-concentration-dependent compensation ratio, see Ref. 13 for details). If we choose $N_{D1} = 3.0 \times 10^{17} \text{ cm}^{-3}$ (which corresponds to the value of the μ_{H1}), one obtains $N_A = 0.6N_{D1} = 1.8 \times 10^{17} \text{ cm}^{-3}$. Moreover, the first donor level may be obtained as $E_C - E_1 = 5 \times 10^{-15} \text{ eV}$ ($N_{D1}^{2/3} = 1.8 \text{ meV}$ (formula from Ref. 14)). According to Ilegems and Montgomery,¹⁵ the saturation temperature for complete donor ionization is $T \sim 1000 \text{ K}$. Extension of the measurement data to this temperature suggests a value of $N_{D2} = 1.0 \times 10^{18} \text{ cm}^{-3}$.

It is found that the corrected mobility data [Fig. 3(b)] are fitted well by solutions of the Boltzmann equations in the relaxation time approximation assuming ionized impurity (ii), deformation potential (dp), piezoelectric (pe), and polar-optical phonon (po) scattering.^{2,4} The good fit is obtained by choosing the above values of $E_C - E_1$, $E_C - E_2$, N_A , N_D , and n_C in the calculation. The scattering constants are taken from Ref. 16, and references therein: acoustic potential $E_1 = 9.2 \text{ eV}$, piezoelectric constant $h_{pz} = 0.5 \text{ C/m}^2$, dielectric constant $\epsilon_\infty = 5.47\epsilon_0$ and $\epsilon_{lf} = 10.4\epsilon_0$, effective mass $m^* = 0.22m_0$, speed of sound $s = 6.59 \times 10^3 \text{ m s}^{-1}$, mass density $\rho = 6.10 \times 10^3 \text{ kg m}^{-3}$, and Debye temperature $T_D = 1044 \text{ K}$.

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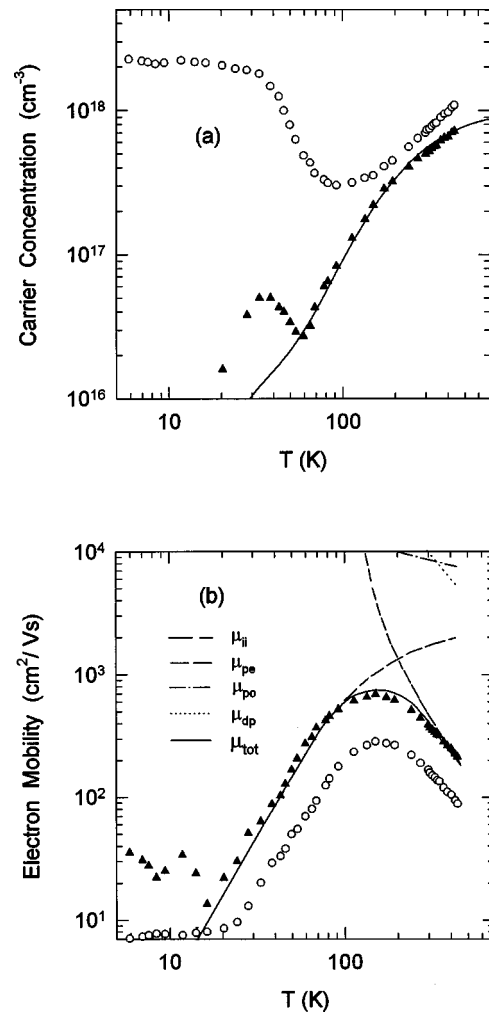


FIG. 3. (a) Temperature dependence of the uncorrected Hall carrier concentration (open circles), and the corrected data (triangles) with the interfacial conduction subtracted. The line shows the model fit to the data as described in the text. (b) Temperature dependence of the uncorrected electron mobility (open circles), and the corrected values (triangles) after the interfacial conduction effect has been subtracted. The line shows the model fit to the data.

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