The depth-profiled carrier concentration and scattering mechanism in undoped GaN film grown on sapphire


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Temperature-dependent Hall (TDH) measurements and confocal micro-Raman spectroscopy have been used to study the free carrier spatial distribution and scattering mechanism in unintentionally doped GaN film grown on the sapphire substrate with the method of metalorganic chemical vapor deposition. Both the TDH data and the depth-profiled Raman spectra agreed with the existence of a nonuniform spatial distribution of free carriers in the GaN film with a highly conductive layer of ~1 μm thickness near the GaN sapphire boundary. With the consideration of this parallel conduction channel adjacent to GaN sapphire boundary, detailed analysis of the TDH mobility data suggests that a relatively high concentration of nitrogen vacancies exists and nitrogen vacancy scattering has an important influence on limiting the electron mobility in the bulk film of the present GaN sample. © 2004 American Institute of Physics. [DOI: 10.1063/1.1763235]

I. INTRODUCTION

GaN has attracted considerable research interest because of its potential applications including blue/ultraviolet light emitting devices, ultraviolet detectors, high-speed, high-temperature field-effect transistors, and high electron mobility transistors. GaN is desirable for high-power, high-speed electronic applications due to its higher breakdown field and larger saturation velocity than GaAs, and also its excellent ballistic conduction under a high electric field (>100 kV/cm). Understanding the electronic transport properties of GaN such as Hall carrier mobility and scattering mechanism is therefore of high importance. Unfortunately such studies are complicated by the poor structural quality of GaN films arising from lattice-mismatched heteroepitaxy (13.8% for sapphire) and the existence of additional parallel conducting channels in the material, such as through impurity bands, interfacial regions, or grain boundaries.

High quality GaN epilayers have been grown on sapphire substrates by introducing a low-temperature grown AlN or a GaN buffer layer. This results in the transport properties of GaN epilayer being shunted by a dislocated interface region with highly conductive properties. A two-layer model, which involves a thin degenerate interfacial layer and the GaN bulk layer, was constructed by Look and Molnar to successfully explain the Hall data although this two-layer model has relied on some assumptions. Using different scanning probe microscopic techniques, Hsu et al. directly observed an interfacial region at the GaN/sapphire boundary having an electron concentration at least an order of magnitude higher than that of the less-conducting bulk film. Evidence for such a degenerate interfacial layer also comes from the depth-profiled temperature-dependent Hall experiments performed by Mavroidis et al. Excess oxygen atoms diffusing from the sapphire substrate and defective microstructure have been suggested to be responsible for the high electron concentration in the interfacial layer.

Raman spectroscopy is not only a dominant method for studying phonons, but also provides a contactless and non-destructive method for determining carrier concentration and mobility. In Raman spectroscopic studies of GaN materials, strong couplings between the longitudinal optical (LO) phonon and the free carrier plasma were observed. The LO phonon-plasmon coupling has the effects of shifting the LO phonon peak to high-frequency side and broadening the line shape. With this principle, Ponce et al. demonstrated how Raman spectroscopy can be used to probe the spatial variation of carrier concentration in Si doped GaN.

In the present work, depth-profiled confocal micro-Raman spectroscopy was used to study the depth distribution of the carrier density across the GaN film grown on the sapphire substrate. Temperature-dependent Hall (TDH) measurements conducted on the same sample were fitted by the two-layer model, in which the first layer is the bulk film and the second one is the degenerate conductive layer. Results from both techniques agree with the two-layer model and the carrier concentrations of the two layers (i.e., GaN bulk layer and interfacial layer) derived from the two techniques coincide well with each other. With considering the highly conductive interfacial layer, analysis of the temperature-dependent mobility in the bulk layer incorporating the influence of various scattering processes reveals an important contribution coming from nitrogen vacancy scattering.

II. EXPERIMENT

The samples used in the present work were unintentionally doped GaN film grown on c-plane sapphire using ammonia (NH₃) and trimethylgallium (TMG) as precursor by metal organic chemical vapor deposition (MOCVD).
sapphire substrate was first heated to 1050 °C in a stream of hydrogen. A ~300 Å thick unintentionally doped GaN buffer layer was grown at low temperature (520 °C). Then the system was heated to 1050 °C and kept for 15 min to anneal the buffer layer. The GaN layer with the thickness of 5 μm was grown at a temperature of 1050 °C. The typical mole ratio of NH3 and TMG was V/III ~2500 during the deposition. More details of the growth procedure can be found in Ref. 20. The samples were cut into square van der Pauw geometry (8×8 mm²). Ohmic contacts were fabricated by evaporating 800 Å Al film onto the GaN epilayer followed by thermal annealing at 750 °C for 2 min under N2 ambient. Good ohmic contacts were verified over the whole measured temperature range. Temperature-dependent Hall effect measurements were carried out in darkness between the temperatures of 4 and 320 K in a magnetic field of 0.5 T using a BIO-RAD HL5580 Hall effect system.

Confocal micro-Raman spectroscopic measurements were carried out by the system consisting of a Spex 750M monochromator with 1800 lines/mm single grating, an Olympus DX40 microscope, a Princeton Spectrum One charge-coupled device detector cooled with liquid nitrogen, and a notch filter. The Raman measurements were performed in back-scattering Z(X,−)Z geometry. The 488 nm line of an Ar⁺ laser operating at a power of 200 mW was used for the light source. The laser beam was focused to a spot size of about 1 μm with the use of a 100× objective lens and thus the spatial resolutions in the x, y, and z directions is of the order of ~1 μm. The instrumental spectral resolution was 1 cm⁻¹. All the Raman spectra were taken at room temperature.

The GaN sample was also etched in H3PO4 at 160°C for 15 min to study the dislocation density. The surface morphology was subsequently analyzed using a tapping mode Digital Instrument III atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

The carrier concentration $n_H$ and the Hall mobility $\mu_H$ measured as a function of temperature for the present GaN sample are shown in Figs. 1(a) and 2(a), respectively. As may be seen, the temperature-independent carrier concentration and mobility are observed at low temperature (<20 K). Because of parallel conduction effects, these measurements do not accurately represent the GaN epilayer properties. For two parallel conduction paths, the carrier concentration can be written as

$$n_H = \frac{(n_{H1}\mu_{H1} + n_{H2}\mu_{H2})}{(n_{H1}\mu_{H1}^2 + n_{H2}\mu_{H2}^2)},$$

where $n_{H1}$ and $\mu_{H1}$ represent the carrier concentration and mobility, respectively, in the GaN bulk film, whose contribution to conduction becomes more significant as the temperature increases, and $n_{H2}$ and $\mu_{H2}$ are associated with a low mobility, metallic channel, which dominates at low temperature. The approach to extract the parameters of each channel from Eq. (1) is to identify the metallic channel either as an impurity band, or as a degenerate layer at GaN substrate interface, i.e., two-layer model in terms of the energetic and spatial distribution of mobile carriers, respectively. In the following paragraph, we find the two-layer model can well describe the TDH data and the depth dependent Raman data.

According to the Raman selection rule and for the $Z(X,−)Z$ configuration used in the present study, $A_1$(LO), $E_2$(low), and $E_2$(high) modes of hexagonal GaN are expected to be observed in the Raman spectra. However, the $E_2$(low) mode is not within the covered spectral range of the present observations made. Micro-Raman spectra of the GaN film at different depth positions are shown in Fig. 3. The parameter “D” is the distance between the GaN film and the position at which the Raman spectrum is taken. All spectra are normalized in intensity by the peak height of the $E_2$(high) mode, and are shifted vertically for easy comparison. A typical Raman spectrum taken at the surface of the GaN film (i.e., $D=5\mu m$) is shown in Fig. 3(a). The dominant lines are the $E_2$(high) (570 cm⁻¹) and $A_1$(LO) (735 cm⁻¹) modes. For the Raman spectrum taken at the interface region $D=1\mu m$ away from the GaN/substrate boundary as shown in Fig. 3(d), the $E_g$ (750 cm⁻¹) mode due to the sapphire substrate is also observed. All of

FIG. 1. Temperature dependence of (a) measured electron concentration $n_H$, (b) Derived electron concentration $n_H$ of GaN bulk film.

FIG. 2. Temperature dependence of (a) measured electron mobility $\mu_H$, (b) Derived electron mobility $\mu_H$ of GaN bulk film.
these Raman signals observed are, in general, agreement with the previous reported Raman modes of epitaxial GaN films.23–27

It is known that the line position of the $E_2$ mode of GaN shifts significantly with the presence of $\sigma_{xx}$ stress in the film.28 It is interesting to note in Fig. 1, the peak positions of the $E_2$ (high) mode were found to be constant at 570±0.5 cm$^{-1}$ for all the Raman spectra taken at different depths. Using the Raman peak position of the $E_2$ mode of a freestanding bulk GaN sample (568 cm$^{-1}$) (Ref. 29) and the formula $\Delta \omega = 6.2 \sigma$ (where $\Delta \omega$ is the frequency shift in cm$^{-1}$ units and $\sigma$ is the biaxial stress in GaP units), the compression stress of the present GaN film is found to be 0.32 GPa. The most likely explanation is that most of the strain caused by the lattice and the thermal-expansion mismatches is re-

It should be noted that $A_1$(LO) peak also shifts due to stress. It was reported that a biaxial compressive stress of 1 GPa will shift the $A_1$(LO) peak toward a higher wave number by 0.8 cm$^{-1}$.37 As was stated in the previous discussion, the GaN film in the present study has a compressive stress about 0.32 GPa when the epilayer is thicker than 1 $\mu$m. This stress is expected to shift the phonon frequency of the $A_1$(LO) mode upwards by 0.25 cm$^{-1}$, an amount which is negligible compared to the observed $A_1$(LO) mode shift of $\sim 3$ cm$^{-1}$ found at the interfacial region. The effect of stress can thus safely be disregarded if the free carrier concentration determination is estimated from the phonon-plasmon coupling mode. In this case, the carrier density $n$ and the drift mobility $\mu$ can be evaluated by a line-shape fitting analysis based on the semiclassical model which involves the consideration of the deformation potential and the electro-optical mechanisms. The line shape of the LO phonon is given by
de
\begin{equation}
I(\omega) = SA(\omega)\text{Im}[\frac{-1}{1-i\varepsilon(\omega)}],
\end{equation}

where $S$ is a proportionality factor,
\begin{equation}
A(\omega) = 1 + 2C(\omega_T^2 - \omega_P^2)\gamma(\omega_T^2 - \omega_P^2 - \omega^2 - \omega_G^2)\varepsilon_T(\omega - \omega_T^2 - \omega_P^2 / \omega^2)\
+ \omega^2\varepsilon_T(\omega + \omega_T^2)\varepsilon_T / \omega^2 (\omega^2 - \omega_T^2),
\end{equation}
\end{equation}

FIG. 3. Room temperature depth-profiled micro-Raman spectra of unintentionally doped GaN film grown on sapphire substrate. The parameter “$D$” denotes the distance away from the GaN/sapphire boundary. The spectra are normalized by the peak intensity of the $E_2$ (high) phonon mode and shifted vertically for comparison. The dotted lines are guide to the eye.
real mobility

m

enough temperature

interfacial layer. The real electron concentration

tion and high mobility, and layer II is taken as the degenerate

tion of the present sample. In this two-layer model, layer I is

n

The sheet Hall concentration

sheet Hall concentration of interfacial layer. 10

function of the measured concentration

confirm, in accordance with previous works, 13,14,43 that there

is a 1 μm width highly conductive and defective interfacial

region adjacent to the GaN/sapphire boundary having an
electron concentration and the mobility of \( n = 8 \times 10^{18} \text{cm}^{-3} \) and \( \mu = 45 \text{cm}^2/\text{V} \text{s} \) respectively.

The presence of the interfacial region with high carrier
contentration suggests employing the two-layer model pro-
posed by Look and Molnar10 to provide a realistic descrip-
tion of the present sample. In this two-layer model, layer I is

taken as the GaN bulk film having a low carrier concentra-
tion and high mobility, and layer II is taken as the degenerate

interfacial layer. The real electron concentration \( n_{\text{II}} \) and the

real mobility \( \mu_{\text{II}} \) of the bulk film can be expressed as a

function of the measured concentration \( n_{\text{II}} \), the measured mobility \( \mu_{\text{II}} \) the interfacial layer thickness \( d \), the Hall param-

ers of the interfacial layer (\( n_{\text{II}} \) and \( \mu_{\text{II}} \)) and \( n_{\text{shII}} \) the

sheet Hall concentration of interfacial layer:

\[
n_{\text{II}} = \frac{(\mu_{\text{II}}^2 n_{\text{II}} - n_{\text{shII}}^2 \mu_{\text{II}})/d^2}{\mu_{\text{II}}^2 + n_{\text{shII}}^2 \mu_{\text{II}}/d},
\]

\[
\mu_{\text{II}}^2 = \frac{\mu_{\text{II}}^2 n_{\text{II}} - n_{\text{shII}}^2 \mu_{\text{II}}/d}{\mu_{\text{II}}^2 + n_{\text{shII}}^2 \mu_{\text{II}}/d}.
\]

In the calculation, the thickness \( d \) of interfacial layer is

taken as 1 μm as revealed by micro-Raman measurement.
The sheet Hall concentration \( n_{\text{shII}} \) can be measured at low

enough temperature (lower than 20 K) as the electrons in the

bulk film freeze out and the measured Hall data are domi-
nated by the contribution from the highly conductive inter-

facial layer. In this case the volume density of electrons in the

interfacial layer is \( n_{\text{II}} = n_{\text{shII}}/d = (7 \pm 0.4) \times 10^{18} \text{cm}^{-3} \).

This carrier concentration coincides with those obtained from

the Raman measurement described in previous para-

graphs (\( n_{\text{II}} = 8 \times 10^{18} \text{cm}^{-3} \)). The observed degenerate and
temperature-independent characteristic of the interfacial

layer [Fig. 1(a)] is also quite consistent with this carrier con-

centration since the Fermi level enters the conduction band

when the carrier concentration is about \( 6 \times 10^{18} \text{cm}^{-3} \).44

The extracted concentration \( n_{\text{II}} \) and mobility \( \mu_{\text{II}} \) of the

bulk film are plotted in Figs. 1(b) and 2(b), respectively. The extracted carrier concentration of the bulk film \( n_{\text{II}} \) at room

temperature is \((0.9 \pm 0.4) \times 10^{17} \text{cm}^{-3} \), which agrees well

with the value \( 1.0 \times 10^{17} \text{cm}^{-3} \) of the near surface carrier

concentration obtained from the capacitance-voltage (\( C-V \))

measurement on the same sample. By fitting the line shape of

the \( A_1(LO) \) Raman peak as described in the previous Raman

section, the carrier concentration at the surface is \( 1.5 \times 10^{17} \text{cm}^{-3} \), which also agrees well with the Hall calculated
data.

In order to analyze the extracted Hall mobility of the

GaN bulk film, the limiting effect imposed by each of the

scattering mechanisms is to be considered. Assuming that the

scattering events are independent of each other, the resultant

mobility is given by the Matthiesen’s rule: \( 1/\mu = \Sigma (1/\mu_i) \),

where \( \mu_i \) are the mobility contributed by the \( i \)th scattering

mechanism. In our first trial of fitting the mobility data \( \mu_{\text{II}} \) in Fig. 2(b), we have included ionized impurity scattering

(\( \mu_{\text{ii}} \)), neutral impurity scattering (\( \mu_{\text{im}} \)), polar optical phonon

scattering (\( \mu_{\text{po}} \)), acoustic deformation potential scattering

(\( \mu_{\text{ap}} \)), and piezoelectric potential scattering (\( \mu_{\text{pe}} \)) with

the use of the well known formulas45,46 and material parameters

of GaN cited in Ref. 47. It is found, however, that the fitting

involving these scattering mechanisms (with \( \mu_i \) plotted as a

function of temperature in Fig. 5) cannot provide a reason-

able fit to the experimental mobility data \( \mu_{\text{II}} \) of the present

GaN bulk film. This implies other scattering mechanisms

have to be considered.

Dislocation scattering in GaN has been studied by

Weimann and Eastman48 and Ng, Pudi, and Moustakas49 These

authors showed that the mobility limited by threading dislo-

cation scattering depends on the dislocation density and the

carrier concentration. Moreover, the mobility \( \mu_{\text{dis}} \) due to

such scattering has a temperature dependence of \( \mu_{\text{dis}} \propto T \).

Dislocation scattering is thus more likely to be dominant at

low temperatures giving it a similar profile to that of ionized

impurity scattering. In our first mobility fitting (with only

TABLE I. Values of the fitting parameters and derived \( n \) and \( \mu \) for Raman \( A_1(LO) \) coupled modes measured at

\( D = 5 \mu m \) and \( D = 1 \mu m \).

<table>
<thead>
<tr>
<th>Raman modes</th>
<th>Fitting parameters</th>
<th>Derived ( n ), ( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \omega_p ) (cm(^{-1}))</td>
<td>( \Gamma ) (cm(^{-1}))</td>
</tr>
<tr>
<td>(1) ( A_1(LO) ) measured at ( D = 5 \mu m )</td>
<td>120</td>
<td>22</td>
</tr>
<tr>
<td>(2) ( A_1(LO) ) measured at ( D = 1 \mu m )</td>
<td>732</td>
<td>110</td>
</tr>
</tbody>
</table>
et al. carried out a selective etching technique using hot H3PO4. They also pointed out, during microscopy was similar to the values obtained by the etching density and the dislocation density. They found that the ef-

The derived electron mobility of GaN bulk film $\mu_{\text{hi}}$ vs temperature, fitted in terms of various scattering mechanisms (as shown in figure). The $\mu_{\text{theory}}$ represents the theory mobility value calculated using Matthiesen’s rule.

$\mu_{\text{ii}}$, $\mu_{\text{ni}}$, $\mu_{\text{po}}$, $\mu_{\text{dp}}$, and $\mu_{\text{pc}}$, deviation between the modeled curve and the experimental data is found to be large at high temperature, which indicates the need for another scattering potential that would effectively limit the mobility at high temperature.

In order to investigate the dislocation density of the present GaN film, AFM images were taken after the sample was wet chemically etched with the use of H3PO4. Recently, Youtsey et al.50,51 demonstrated that the whisker density obtained by selectively etching GaN are very close to the effective dislocation density. Visconti et al.52 carried out a series of experiments to clarify the relation between the etch pit density and the dislocation density. They found that the effective dislocation density obtained by transmission electron microscopy was similar to the values obtained by the etching technique using hot H3PO4. They also pointed out, during wet etching, a careful balance must be made to ensure that every defect is delineated, and that no overetching takes place to cause merging which would lead to an underestimation of the defect density. Figure 6 shows the surface morphology of the present GaN sample observed by AFM after the sample being etched in H3PO4 for 15 min at 160 °C. By counting the number of etch pits per unit area, the dislocation density of the present GaN sample was found to have a value of $3 \times 5 \times 10^8$ cm$^{-2}$. This value is relatively low as compared with the dislocation density of $\sim 10^{10}$ cm$^{-2}$ present at the poorly matched GaN sapphire interface. From the viewpoint of the two-step MOCVD growth technique which was used in fabricating the present samples, it can be concluded that the dislocations are mainly confined to the GaN/sapphire interfacial region as the growth of the low-temperature buffer layer is introduced.

The dislocation density of the present sample revealed from the AFM technique with wet etching is $3 \times 5 \times 10^8$ cm$^{-2}$, while the scattering at charged dislocation lines only becomes significant for dislocation density above $10^9$ cm$^{-2}$. This implies that dislocation scattering is not likely to be a significant scattering process in the GaN bulk film.

Zhu and Sawaki53 proposed that nitrogen vacancy ($V_N$) scattering should be taken into account when analyzing the electron mobility data in GaN films grown by MOCVD. Although theoretical calculation reveals that for $n$-type GaN the formation energy of $V_N$ is large i.e., about 4 eV,54 it does not exclude the possibility that the GaN materials have relatively high nitrogen vacancy concentration under certain growth conditions. Moreover, technologically it is likely that $V_N$ is present during the growth process because of the very high nitrogen equilibrium pressure at the high growth temperature. Using a square-well potential to describe the nitrogen-vacancy-induced scattering potential, Zhu and Sawaki53 showed that the mobility ($\mu_{V_N}$) caused by this scattering follows $\mu_{V_N} \propto T^{-1/2}$ and thus this kind of scattering has the derived form of being dominant at high temperatures. In addition, Chua et al.55 reported that $V_N$ were created in stoichiomertic GaN film by plasma exposure and also showed the mobility limited by nitrogen vacancy scattering follows $\sim T^{-1/3}$, which is close to the result predicted by Zhu and Sawaki53.

In the final mobility fitting (shown in Fig. 5), $V_N$ scattering was taken into account by including the $V_N$ limiting mobility53

$$\mu_{V_N} = \frac{9}{16\sqrt{3}} \frac{h^4}{m^{5/2}N_{V_N}} \frac{1}{U_{0}^{2}} \frac{e^{\Delta U}}{(k_BT)^{1/2}}. \tag{7}$$

The compensated acceptor concentration ($N_A$), and the nitrogen vacancy concentration ($N_{V_N}$) are treated as the free parameters in the fitting process. A least squares fit of the mobility data yielded a good agreement over the entire temperature range with fitted values of $N_A = (5.8 \pm 0.5) \times 10^{16}$ cm$^{-3}$ and $N_{V_N} = (1.7 \pm 0.5) \times 10^{17}$ cm$^{-3}$. The results indicate that the concentration of nitrogen vacancies is relatively high in the bulk film of the present GaN sample and nitrogen vacancies play a significant role in limiting the electron mobility.

With the charge neutrality equation, the donor concentration $N_D$ and the donor ionization energy $E_D$ are given by

$$N_D + N_A = N_{V_N} + N_{A}^{\text{imp}}.$$
Since for GaN, the experimentally determined screening parameter depends on the concentration of compensating acceptors. Si as possible residual donors in the present sample. The unscreened donor binding energy can be calculated as $E_D = 24.4 \text{ meV}$. This value is close to the values of Si or O shallow donors reported in the literature. This implies O or Si as possible residual donors in the present sample.

As the fitting described in previous paragraphs gives the concentration of compensating acceptors $N_A = 5.8 \times 10^{10} \text{ cm}^{-3}$ in the present sample, the acceptor to donor ratio is $N_A/N_D = 0.31$. Considering the mobility limiting mechanisms of ionized impurity scattering, piezoelectric scattering, acoustic phonon, and polar optical phonon scattering, Chin, Tansley, and Osotchan have calculated the carrier mobility of GaN as a function of temperature for different $N_A/N_D$ ratio. It is noticed that with the present $N_A/N_D$ ratio, the calculated mobility given by Chin, Tansley, and Osotchan is higher than the experimental data obtained in the present study. This implies the observed low carrier mobility in the present study is not only due to the heavy compensation but is also a consequence of other scattering processes, such as dislocation, stacking fault scattering (in the interfacial region) and nitrogen vacancy scattering (in the bulk film).

**IV. CONCLUSION**

In conclusion, we have studied the unintentionally doped GaN films grown on sapphire with the use of the depth-profiled micro-Raman spectroscopy, the AFM technique combined with wet etching, and temperature-dependent Hall measurements. The decrease of the peak intensity and the asymmetrical broadening of $A_1(LO)$ phonon line taken at the depth close to the near GaN/sapphire interface region ($D \approx 1 \mu\text{m}$) indicates the presence of a highly conductive interfacial layer. The carrier concentrations of the bulk film and also the interfacial layer were determined by fitting the line shape of the $A_1(LO)$ coupled modes. Based on the presence of this conductive interfacial layer, a two-layer model has been used to analyze the temperature-dependent Hall data. The carrier concentration and the mobility of the GaN/sapphire interfacial region and GaN bulk film determined by the Raman method are found to agree well with those obtained from Hall data analysis. Detailed mobility analysis strongly suggests that nitrogen vacancy scattering has an important electron mobility limiting effect in the GaN bulk film. The Hall data also confirm that dislocation scattering is dominant in the interfacial region, but is not the important scattering mechanism in the GaN bulk film, which coincides with the low dislocation densities found in the GaN bulk film revealed by the chemical etching method.

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