Effect of dislocations on luminescence properties of silicon-doped GaN grown by metalorganic chemical vapor deposition method

Jahangir Alam
Department of Electrical Engineering, Howard University, 2300 Sixth St. NW, Washington, DC 20059

Ravi Bathe and R. D. Vispute
Department of Physics, University of Maryland, College Park, Maryland 20742

John M. Zavada
Army Research Laboratory, Army Research Office, P.O. Box 12211, Research Triangle Park, North Carolina 27709-2211

Cole W. Litton
Electronic Research Directorate, U.S. Air Force Research Laboratory, Wright Patterson AFB, Ohio 45433

Agis A. Iliadis
Department of Electrical and Computer Engineering, University of Maryland, College Park, Maryland 20742

S. Noor Mohammad
Department of Electrical Engineering, Howard University, 2300 Sixth St. NW, Washington, DC 20059

(Received 24 July 2003; accepted 12 January 2004; published 4 March 2004)

The effect of dislocations on the structural and electro-optic characteristics of \( n \)-GaN has been studied. X-ray diffraction, Hall measurement, photoluminescence spectroscopy, Raman spectroscopy, and transmission electron microscopy (TEM) have been performed to understand the interdependence of strain, dislocation, and doping concentration. The most remarkable observation of the study is the blueshift observed at a doping level \( N_D \sim 10^{18} \text{ cm}^{-3} \) as a result of the relaxation of strain. The TEM results reveal a higher dislocation defect density at lower doping levels \((\lesssim 10^{17} \text{ cm}^{-3})\) than at moderate doping levels. Blueshift is found to result from the redistribution of the dislocation density due to the reduction in strain at a certain optimum doping level(s). This distribution of the dislocation is such that there are virtually no dislocations at some locations, as evident from the sample MD27 with doping \( \gtrsim 10^{19} \text{ cm}^{-3} \). © 2004 American Vacuum Society. [DOI: 10.1116/1.1667509]

I. INTRODUCTION

III–V nitrides have recently emerged as important materials for various devices.\(^1\) These III–V nitrides are indeed some of the most intriguing materials for blue-green light-emitting diodes and blue-green lasers. Despite the rapid development in III–V nitride growth and device technologies, most of today’s nitrides are still grown on substrates to which they are both lattice and thermally mismatched. Sapphire is the most commonly used substrate for III–V nitride growth. Thin films of III–V nitrides thus grown on sapphire substrate suffer from high concentration of structural defects, such as grain boundaries, dislocations, and point defects. The defects are further modified when the materials are doped \( n \)-type or \( p \)-type. In this article, we carry out an in-depth investigation of the effects of Si doping on the optical energy shifts of \( n \)-GaN grown on sapphire substrate by the metalorganic chemical vapor deposition (MOCVD) method. Several different characterization techniques are employed for this investigation. The strain dependencies of bandgap and exciton energies associated with transitions from three separate valence bands (\( \Gamma_9, \Gamma_7, \) and \( \Gamma_7 \) for A, B, and C bands, respectively) are also addressed.

II. EPITAXIAL GROWTH

For the present study, wurtzite \( n \)-GaN layers were grown by MOCVD vertical flow reactor on (0001) sapphire substrates \((\sim 400 \mu \text{m})\). The substrates were cleaned with hydrogen plasma and then degreased with organic solvents prior to the growth. They were etched in a hot solution of \( \text{H}_2\text{SO}_4 \) and \( \text{H}_3\text{PO}_4 \) \((\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4=3:1)\) for about 20 min, rinsed in deionized water, and then dried by blowing filtered nitrogen. The sapphire was nitridated for about 15 min at 800 °C. Prior to the GaN epitaxial growth, an undoped GaN buffer layer, about 300 Å thick, was grown on the sapphire substrate at a temperature of 545 °C. This was followed by the growth of a 1.6 \( \mu \text{m} \) thick GaN epitaxial layers \((\text{MD13, MD25, MD26, and MD27})\) doped with Si to four different donor concentrations \((N_D)\). Silane was the source of Si dopant atoms. Different doping levels were achieved by varying silane flow rate into the growth chamber. All other growth parameters were kept constant during the GaN growth with a particular doping level.

III. MATERIALS CHARACTERIZATION AND DISCUSSION

Hall measurement yielded the carrier concentrations. Although not conclusively confirmed, the residual acceptor
concentration ($N_A$) appeared to be low. X-ray diffraction (XRD) measurements were performed using Cu $K\alpha_1$ radiation. Photoluminescence (PL) was excited by the 325 nm line of a He-Cd laser and collected in a front surface configuration. The samples were fixed on a cryostat sample holder using rubber glue, and the temperature was regulated down to 6 K from 300 K using a closed cycle liquid He cryostat. The structural characteristics of the films were analyzed by cross-sectional transmission electron microscopy (XTEM).

A. XTEM characterization

GaN is under biaxial strain. There are two sources of this strain in GaN grown on the sapphire substrate: intrinsic lattice mismatch between the two crystals and the differences in thermal expansion coefficients between these two crystals. Both are important, but it is the difference in thermal expansion coefficient that gives rise to the compressive stress observed at room temperature. The biaxial strain is responsible for the dislocations formed near the interface during cooling down after the growth. In light of this, the structural qualities of various films were analyzed and evaluated using TEM micrographs, XRD patterns, Raman spectra, and PL spectra. TEM patterns of two representative samples (MD25 and MD27) are shown in Fig. 1. The threading dislocation density $\rho_{TD}$ and the free carrier concentration $n_{FC}$ of various layers are presented in Table I. One can see from this table that $\rho_{TD}$ increases with increasing $n_{FC}$ until $n_{FC} = 2.6 \times 10^{15}$ cm$^{-3}$ for MD26. It then decreases with further increase in $n_{FC}$, being $3 \times 10^9$ cm$^{-2}$ for MD27 as compared to $5 \times 10^9$ cm$^{-2}$ for MD25. In addition, it is clustered. The dislocations in MD13 are grouped together rather than being at scattered positions. In contrast, in MD25, they are almost uniformly distributed throughout the sample. As revealed by the XTEM both (edge and screw/mixed) dislocations constitute much of the dislocations distributed across the sample. The higher $\rho_{TD}$ in MD25 does not conform to the observation that $\rho_{TD}$ decreases with increasing doping, as reported earlier. $^{3-8}$ Pyramidal defects, primarily those parallel to the surface, are seen in layers, discussed here. Nanopipes are also seen above some of these pyramidal defects.

B. XRD characterization

The full width at half-maximum (FWHM) of the XRD patterns shows a gradual decrease for layers with increasing doping concentration. This is because, $^9$ with increasing Si concentration (for example, $n_{FC} = 3 \times 10^{15}$ cm$^{-3}$ for moderately Si-doped samples), the $c$ value decreases, which causes an increment in $a$ in the basal plane. The increment in $a$ causes the formation of dislocations in the basal plane, leading to a decrease in the compressive stress, as observed in our films. In fact, as dislocations are formed, the strain is relieved, and the lattice constant approaches the relaxed value. Thus, these are the dislocations that result in decreased strain. As our sample was a 1.6 $\mu$m thick epilayer, we chose 5.1850 Å to be the relaxed value for the lattice constant $c$. The $c$ values for various layer structures are presented in Table I. From this table, we note that the lattice constant $c$ for MD25 decreases to a value of 5.1759 Å from its relaxed value of 5.1850 Å. For MD27, however, the value increases to 5.1892 Å from its relaxed value of 5.1850 Å.
Notably, MD27 exhibits higher Si doping concentration. The shrinkage in c of MD25 caused by Si doping results in relaxation of the stress. On the other hand, the increase in c of MD27 accompanies a pronounced shrinkage in the lattice constant a in its basal plane. Due to this shrinkage of a, there is a bending of threading dislocations needed to accommodate the changes in the strain. Density of planar defects increases with increasing Si doping.\(^{10}\) The interaction of these planar defects with vertical line dislocations might have also contributed to the bending and even redistribution of the line dislocations, resulting in segments of misfit dislocations.\(^ {11}\)

According to Sugiura,\(^ {12}\) the straight threading dislocations parallel to the c axis in GaN occur predominantly on (0001) basal planes. These basal dislocations are very mobile, and hence the change in stress and strain due to Si doping leads them to move and to regroup to accommodate the changes. This is evident from the TEM micrograph of MD27 where, in certain locations, there are no dislocations at all, above the segments lying in the c plane, and in some other locations these are clustered together. The regrouping of dislocations appears indeed to be responsible for a change in strain/stress conditions. A reduction of \(\rho_{TD}\) in MD27 compared to that in MD25 might have brought about a strain relaxation. This very relaxation is the actual cause of the blueshift in MD27.

### C. Photoluminescence characterization

Figure 2(a) shows the 6 K PL spectra of various samples. The FWHM of these samples are listed in Table I. This table indicates that, for the low-doped sample MD13, the FWHM is 7.16 meV and the neutral donor bound exciton (D\(^0\)X) peak is 3.4791 eV. Figure 2(b) shows the 30 K PL spectrum of the sample MD13. From this figure, one may note that the D\(^0\)X peak is gradually reduced and has lower intensity. However, two distinct shoulders are created on the high-energy side of the spectrum, which are labeled, respectively, as FX\(_A\) (free exciton A) at the peak position of 3.4879 eV, and FX\(_B\) (free exciton B) at the peak position of 3.4968 eV. The separation between FX\(_A\) and FX\(_B\) is about 8.9 meV, and that between FX\(_A\) and the donor bound energy peak at 3.4797 eV is 8.2 meV. The separation of the FX\(_B\) from the D\(^0\)X peak is 17.1 meV. The separation between the bound exciton and the two free excitons is a measure of the ionization energies of the two free excitons separated by 8.9 meV. Unfortunately, the two shoulders are not well-resolved at low temperature. However, as the temperature increases, the FX\(_A\) and FX\(_B\) increase gradually, but at the expense of the binding energy of D\(^0\)X. At 110 K, the D\(^0\)X disappears, indicating a complete ionization of the D\(^0\)X into FX and D\(^0\).

From Table I, it can be seen that the FWHM of MD27 is higher due to higher doping concentration. The broadening, leading to higher FWHM, may be attributed to the band tailing arising from the potential fluctuation of the tail states of band edges. Apart from Si doping, the residual acceptors are also thought to contribute to the luminescence broadening, yielding larger linewidth. Due to gradually increasing Si doping, there is an in-plane tension\(^ {9,14}\) in the film. Thus, at a doping level above 4.8 \(\times 10^{18} \text{ cm}^{-3}\), the PL peak moves back to higher energies and is broadened. It appears that the in-plane strain increases with Si doping, and the transition from the compressive to the tensile strain occurs at a doping level beyond \(10^{18} \text{ cm}^{-3}\). Increasing disorder at a higher doping level generates potential fluctuations proportional to \((N_D + N_A)^{1/2}\) in the sample. Generally, if the compensation is heavy, \(N_D + N_A\) is much higher than the carrier concentration. On the other hand, if the compensation is low or moderate, \(N_D + N_A\) is comparable to the carrier concentration. Thus, higher compensation causes greater potential fluctuation for a fixed carrier concentration. Accordingly, the broadening of the PL peak is shaped, and the doping level for blueshift is determined. In our case, the blueshift occurs at a doping level \(n_{FC} \approx 4.8 \times 10^{18} \text{ cm}^{-3}\) for MD27.

In general, as the doping concentration increases, the carrier concentration also increases, which accompanies an increase in the intensity of the PL peak. The undoped GaN films with lower doping concentration suffer from higher destructive influence of the nonradiative centers, and hence have much weaker UV luminescence intensity. For this reason, the UV PL peak intensity of MD25 is lower than that of MD27. Further, the residual strain of MD25 arising from Si doping is high enough to cause an increase in \(\rho_{TD}\) to 5 \(\times 10^{16} \text{ cm}^{-2}\), and consequently a redshift in the PL peak. The PL peak intensity also increases in this sample. However, this PL peak moves to a lower energy position of 3.4780 eV, showing a redshift. In contrast, the PL peak of the heavily doped MD27 moves to higher energy position of 3.4830 eV, showing a blueshift. MD27 exhibits the blueshift of 4.3 meV with respect to MD13. As argued earlier, depending on compensation and growth conditions, the limit of the doping

### Table I. Experimental parameters for various layer structures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier conc (n_{FC}) ((\text{cm}^{-3}))</th>
<th>Dislocation density (\rho_{TD}) ((\text{cm}^{-2}))</th>
<th>(c^a) ((\text{Å}))</th>
<th>PL FWHM ((\text{meV}))</th>
<th>PL peak ((\text{eV}))</th>
<th>Raman peak (E_2^s) ((\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD13</td>
<td>(5.0 \times 10^{16})</td>
<td>(1.0 \times 10^9)</td>
<td>5.1799</td>
<td>7.000</td>
<td>3.4797</td>
<td>567.8</td>
</tr>
<tr>
<td>MD25</td>
<td>(7.0 \times 10^{17})</td>
<td>(4.9 \times 10^9)</td>
<td>5.1759</td>
<td>9.1400</td>
<td>3.4780</td>
<td>566.8</td>
</tr>
<tr>
<td>MD26</td>
<td>(2.6 \times 10^{18})</td>
<td>(5.0 \times 10^9)</td>
<td>5.1735</td>
<td>12.300</td>
<td>3.4765</td>
<td>567.0</td>
</tr>
<tr>
<td>MD27</td>
<td>(4.8 \times 10^{18})</td>
<td>(3.0 \times 10^9)</td>
<td>5.1892</td>
<td>13.095</td>
<td>3.4830</td>
<td>567.6</td>
</tr>
</tbody>
</table>

\(^a\)5.1850 Å is the relaxed value.

This is evident from the TEM micrograph of MD27 where, in certain locations, there are no dislocations at all, above the segments lying in the c plane, and in some other locations these are clustered together. The regrouping of dislocations appears indeed to be responsible for a change in strain/stress conditions. A reduction of \(\rho_{TD}\) in MD27 compared to that in MD25 might have brought about a strain relaxation. This very relaxation is the actual cause of the blueshift in MD27.
level, where the blueshift sets in, varies from sample to sample. For example, it was greater than $10^{19}$ cm$^{-3}$ for layers of Lareoux et al., and was between $10^{18}$ and $10^{19}$ cm$^{-3}$ for layers of Meister et al.

**D. Raman characterization**

Raman scattering measurements were made on all four samples, and the results are presented in Fig. 3. The corresponding peak positions of these spectra are listed in Table I. The reliability of these data for each sample is verified by measurements at several spots. Figure 3 indicates that the thermal biaxial strain, arising from unequal thermal expansion coefficients of the substrate and the GaN film, introduces stresses, as observed by the shift of the E$_2$ phonon modes of the Raman spectra. Point defects might have introduced an internal hydrostatic strain that can be compressive or expansive depending on the size of the atoms and the extended defects involved. Native defect formation in GaN is strongly influenced by compressive stress arising from unequal covalent radii of Ga and N atoms. The line position of the E$_2$ phonon mode is known to be independent of the carrier density, but it shifts depending upon the residual stress in the material. Because of this stress, E$_2$ line position varies almost continuously, even if different samples are grown at identical temperature. This is consistent with the observation that there might be a linear correlation between $\rho_{TD}$ and the E$_2$ and E$_1$ phonons.

If $\sigma$ is the biaxial thermal stress in Gpa$^{-1}$ and $\Delta \omega$ is the Raman shift in cm$^{-1}$, then this shift as a function of layer thickness, as given by Tripathy et al., is $\Delta \omega = 4.86 \sigma$ (cm$^{-1}$ Gpa$^{-1}$) for a layer thickness of 0.1 to 4 $\mu$m. As given by Kozawa et al., it is $\Delta \omega = 6.2 \sigma$ (cm$^{-1}$ Gpa$^{-1}$) for a layer thickness of 2.5 to 50 $\mu$m; and as given by Kim et al., it is $\Delta \omega = 3.93 \sigma$ (cm$^{-1}$ Gpa$^{-1}$) for a layer thickness of 10 to 240 $\mu$m. Since our film thickness was 1.6 $\mu$m, we made use of the relationship by Tripathy, which yielded the E$_2$ values given in Table I. There is a gradual reduction of calculated $\sigma$ values (not shown) for all the samples except MD27. The $\sigma$ for MD27 is higher compared to that of MD26. Thus, our Raman spectra for MD27 show an upward shift of the E$_2$ phonon position by about 0.6 cm$^{-1}$ compared to MD26. It supports also a reduction in the biaxial strain arising from in-plane compression due to higher doping. Our XRD results support it, as well. This very change in biaxial strain causes a blueshift in the PL peak of MD27.
E. Comparative discussions

The near-band-edge PL redshift might actually have been dictated by several causes. Thus, there is confusion about the origin of observed donor bound excitonic transition lines, culminating in the belief that the bandgap narrowing (BGN) effect is the main cause for this. The present data (XRD, PL, and the Raman) strongly emphasize that the PL blueshift of the MD27 is indeed due to changes in stress caused by Si doping. Specifically, the relaxation of the strain accompanying a change in the stress by Si doping around 4.8 \times 10^{19} \text{cm}^{-2} \text{ and higher is responsible for the blueshift. The shift towards the lower energy position in MD25 may probably be due to BGN effect of the energy bandgap.}

Hall mobility is strongly dependent on the structural defects, such as dislocations, twists, etc. Among them, dislocations play a significant role as scattering centers. Dislocations are also known to be nonradiative centers in GaN at room temperature. These are negatively charged. Dangling bonds are formed in the dislocation centers, and act as negatively charged lines. Thus, a negative space-charge region is created around these dislocations, which scatters electrons traveling across the material and reduces their mobility. These dislocations also act as trapping centers for holes, thus forming nonradiative centers. MD25 has a dislocation density of $5 \times 10^9 \text{cm}^{-2}$, which is higher than the dislocation density $3 \times 10^9 \text{cm}^{-2}$ of MD27. Because of this, the mobility in MD25 should be low. In the present work, this mobility is indeed $202 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, as compared to the mobility $195 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ of the much more highly doped sample MD27. Dislocations might have acted as scattering centers more dominantly in MD25 than in MD27, reducing the electron mobility in MD25.

IV. YELLOW EMISSION

The 6 K PL spectra of samples MD13, MD25, MD26, and MD27, obtained over a wide energy range (1.7 to 3.5 eV) are depicted in Fig. 4. Considering the energy position of the PL micrograph, it is evident that the yellow emission arises from the Ga and N vacancies formed during growth. As may be noted from Fig. 4, this emission corresponds to the energy range of 1.8 to 2.6 eV of the PL spectra of all the samples. The peak value for this is highest for MD27 and lowest for MD13. The yellow emission depends primarily on the doping level. To reiterate, while the doping level for MD27 is the highest, that for MD13 is the lowest. The microscopic origin of the yellow emission is probably the gallium vacancy $V_{Ga}$ and most of these defects exist near the interface region between the buffer layer (or the substrate) and the GaN epilayer. The optical transitions between the impurity or defect state energy levels produce this yellow band. Si doping causes the occupation of the Ga vacancies ($V_{Ga}$). Thus, the yellow emission intensity ($I_{YL}$) should have decreased due to increased Si doping. However, it has not happened; rather, $I_{YL}$ increases and the peak widens owing to the increased Si doping level. The UV emission intensity ($I_{UV}$) also increases with increasing doping level. However, the ratio $R_{YL/UV} = I_{YL}/I_{UV}$ decreases with the increasing doping level. This suggests that some, but not all, of the Si atoms can occupy the Ga vacancies. It also gives a quantitative measure of the compensation. The $R_{YL/UV}$ for MD25 is higher than those for MD27 and MD13. During our growth, the flow level of ammonia was kept constant, while the silane flow rate was increased to increase the doping density. As a result, some new nitrogen vacancies $V_N$ might have been formed. With Si occupying the positions of the gallium vacancies $V_{Ga}$, the density of the nitrogen vacancies is higher than that of the gallium vacancies. Thus, while the occupancy of the gallium vacancies by Si leads to an enhancement of free carrier concentration, and consequently to an increase in UV emission, the formation of the nitrogen vacancies also helps to increase the UV emission.

V. CONCLUSION

In conclusion, the effect of dislocations on the luminescence properties of the MOCVD-grown $n$-GaN has been investigated. It is observed that the intrinsic transition energies depend on the strain, which varies with the intentional doping concentration $N_D$ and shifts the PL spectra. In addition, the exciton transitions are closely related to the degree of the strain. TEM, XRD, PL, Raman, and Hall measurement studies show that the strain, dislocation and doping concentration are all interdependent. The most striking feature of the study is the observation of blueshift at $N_D \approx 10^{18} \text{cm}^{-3}$ as a result.
of the relaxation of strain. The TEM results reveal higher dislocation defect density at lower doping levels ($\sim 10^{17}$ cm$^{-3}$). However, this decreases at moderate doping levels. blueshift results from a redistribution of the dislocation density due to reduction in strain at a certain optimum doping level. Owing to this redistribution, there are virtually no dislocations at some locations in the sample MD27 with doping $\geq 10^{18}$ cm$^{-3}$.

ACKNOWLEDGMENTS

The authors wish to thank Dr. K. A. Jones, M. A. Derenge, Dr. Z. Liliental-Weber, Dr. Jacek Jasinsky, and Dr. Jaime Freitas for illuminating technical discussions. The research was supported by Ballistic Missiles Defense Organization and the Army Research Laboratory, Adelphi, MD.

1For a recent review of issues germane to GaN-based devices, see S. Noor Mohammad and H. Morkoc, J. Prog. Quantum Electron. 20, 361 (1996).