Spectroscopic signatures of native charge compensation in Mg doped GaN nanorods

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Abstract
We study the native charge compensation effect in Mg doped GaN nanorods (NRs), grown by Plasma Assisted Molecular Beam Epitaxy (PAMBE), using Raman, photoluminescence (PL) and x-ray photoelectron spectroscopies (XPS). The XPS valence band analysis shows that upon Mg incorporation the $E_F - E_{VBM}$ reduces, suggesting the compensation of the native n-type character of GaN NRs. Raman spectroscopic studies of these samples reveal that the line shape of the longitudinal phonon plasmon (LPP) coupled mode is sensitive to Mg concentration and hence to the background n-type carrier density. We estimate a two order of native charge compensation in GaN NRs upon Mg-doping with a concentration of $10^{19}-10^{20}$ atoms cm$^{-3}$. The atomistic origin of this compensation effect in these GaN nanorod samples is discussed.

Epitaxially grown semiconductor nanostructures such as quantum dots, nanowires and nanorods of III-V materials have been investigated extensively in the literature [1–4]. The interest to study these nanostructured materials lies in the fact that they offer an extra degree of freedom to manipulate their properties in comparison to their bulk form. The enhanced performance of nanostructure based devices is partly due to the effective lateral stress relaxation as a consequence of the presence of facet edges and sidewalls. These crystal facets also minimize or eliminate the formation of dislocations, and consequently leads to the fabrication of nearly defect-free III-V semiconductor nanostructures with large surface to volume ratios [5, 6]. 1D Nanorods(NRs) offer several advantages over planar structures, in terms of reduced dislocation density [7, 8], lower polarization field [9], and enhanced light output efficiency [10]. This approach can also reduce the cost of LED fabrication on large-area Si substrates. Thus, growth, characterization and optimization of single crystalline nitride NRs have been of great interest, which has the tremendous potential for technological applications.

Various techniques such as Hall, C-V and other measurements which are employed to study the electronic properties such as carrier density, mobility etc. of semiconducting films, require preparation of Ohmic contacts to the films, which is very difficult to achieve for nanostructures due to their morphological discontinuity and their small dimensions. Raman spectroscopy is a very powerful technique to study material properties of nitride semiconductors. It is well known that unintentionally doped GaN films are intrinsically n-type and the background carrier densities are of the order of $10^{17}-10^{19}$ cm$^{-3}$. The plasmonic oscillations of such free electrons couple with longitudinal optical (LO) phonon modes via its associated longitudinal electric field, giving rise to longitudinal phonon-plasmon (LPP) coupled modes, which are Raman active. Behaviour of this mode drastically changes with carrier concentration, enabling a contactless, local, optical probe of carrier concentration. The shifts of the peak positions of the LPP modes upon Mg doping have been reported earlier [11], but the effect on line shape is not yet clearly probed.

In this work we synthesize single crystalline (wurtzite) hexagonal shaped GaN NRs on Si (111) surface using plasma assisted molecular beam epitaxy (PA-MBE). The Mg and Ga flux rates are varied by adjusting respective K-cell temperatures and monitored by measuring the beam equivalent pressure (BEP). Concentrations of Mg incorporated in these samples are estimated by SIMS measurements as reported in our previous work [12]. Other growth parameters employed can be found elsewhere [12]. The morphology of the grown films are
determined ex-situ using a field emission scanning electron microscope (FESEM, Quanta 3D operating at 20 kV). The optical properties of the films at RT are studied by photo-luminescence spectroscopy (PL, Horiba Jobin Yvon) using a Xenon lamp source for excitation and Raman spectroscopy is performed with an Ar laser of wavelength 514 nm in the back scattering geometry \( z(y, - z) \). The electronic structure of the films are characterized by x-ray photoelectron spectroscopy (XPS) with Al-K\( _{\alpha} \) (1 486.7 eV) source.

The cross section FESEM images of the grown samples as shown in figures 1(a)–(d), reveal the formation of well aligned uniform NRs [12]. A thorough discussion on their structural (single crystallinity) and morphological analysis and Mg dopant concentration has been reported earlier [12]. The effect of Mg doping on electronic structure is characterized by XPS valence band spectra and is shown in figure 1(e), where the position of Fermi level \( (E_F) \) with respect to Valence Band Maximum \( (E_{\text{VBM}}) \) is the signature of the type and concentration of the charge carrier. We find that for sample A (undoped), \( E_F \) is at 2.05 eV above \( E_{\text{VBM}} \) indicating native n-type character of pristine GaN NRs, as expected in GaN growth. Upon Mg incorporation in the NRs the Fermi level moves towards VBM as the \( |E_F - E_{\text{VBM}}| \) reduces to 1.68 and 1.60 for samples B and C, respectively, clearly showing that the native n-type character is being compensated upon Mg doping. Also for sample D the \( |E_F - E_{\text{VBM}}| \) is observed at 1.41 eV suggesting that the sample D has become p-type with free holes.

The Raman spectra acquired at RT for all the four samples are shown in figure 2. Presence of \( E_2(2\text{LO}) \) and \( E_2(\text{low}) \) at \( \approx 567 \text{ cm}^{-1} \) and \( \approx 144 \text{ cm}^{-1} \) (not shown here), \( E_2(\text{TO}) \) and \( A_1(\text{TO}) \) at \( \approx 557 \text{ cm}^{-1} \) and \( \approx 532 \text{ cm}^{-1} \), respectively, confirms single crystalline wurtzite phase of these GaN films. Along with the expected peaks from GaN, a local vibrational mode (LVM) appears at 662 cm\(^{-1}\) for Mg doped samples, which is attributed to the Mg-N bond [13]. For single crystalline and relaxed thin films, the \( A_1(\text{LO}) \) and \( E_2(\text{LO}) \) phonon frequencies are reported to be 734 cm\(^{-1}\) and 741 cm\(^{-1}\), respectively [14] with a deviation of 1–2 cm\(^{-1}\) [15, 16]. Since in the scattering geometry \( z(y, - z) \) only \( A_1(\text{LO}) \) is allowed, the two different modes observed in our studies at \( \approx 721 \text{ cm}^{-1} \) and \( \approx 738 \text{ cm}^{-1} \) are identified as surface optical (SO) phonon peak and longitudinal phonon-plasmon (LPP+) mode, respectively [17]. The SO phonon peak is generally absent in bulk GaN films but is quiet prominent in the NRs due to the relatively large surface to volume ratio. Raman line profile of the LPP coupled mode is given by the following equations [18]

\[
I(\omega) = \text{const}A(\omega)\text{Im}[\epsilon^{-1}] \tag{1}
\]

where \( \omega \) is Raman shift, \( \epsilon(\omega) \) is dielectric function and \( A(\omega) \) is of the following form

\[
\begin{align*}
A(\omega) &= 1 + 2C\frac{\omega_{\text{TO}}^2}{\delta}[\omega_p^2 \gamma (\omega_{\text{TO}}^2 - \omega^2) - \omega^2 \Gamma(\omega^2 + \gamma^2 - \omega_p^2)] \\
&+ C^2 \omega_p^4 [\gamma (\omega_{\text{TO}}^2 - \omega_p^2) + \Gamma(\omega_p^2 - 2\omega^2)] \\
&+ \omega^2 \Gamma(\omega^2 + \gamma^2) [\frac{\omega_{\text{TO}}^4}{\delta(\omega_{\text{TO}}^2 - \omega_p^2)}].
\end{align*}
\tag{2}
\]
where

\[ \delta = \omega_p^2 \left( (\omega \Gamma)^2 + (\omega_{TO}^2 - \omega_p^2)^2 \right) + \omega^2 T (\omega^2 + \gamma^2) (\omega_{LO}^2 - \omega_{TO}^2), \]

(3)

where \( C \) is the Faust-Henry coefficient, \( \omega_{LO} \) and \( \omega_{TO} \) represent the LO and TO phonon frequencies of \( A_1 \) phonon mode, respectively. \( \gamma \) and \( \Gamma \) are the plasmon and phonon damping constants, respectively. \( \omega_p \) is the plasma frequency given by following formula

\[ \omega_p = \sqrt{\frac{4\pi n e^2}{\epsilon_\infty m^*}} \]  

(4)

where \( n \) is the electron carrier density, \( m^* \) is the effective mass of the electron and \( \epsilon_\infty \) is the high frequency dielectric constant. The dielectric function \( \epsilon(\omega) \) in equation (1) is given by:

\[ \epsilon(\omega) = \epsilon_\infty \left[ 1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\omega \Gamma} - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \right] \]  

(5)

The schematic representation of equation (1) is shown in figure 3. The frequency of the LPP mode and its line width are dependent on carrier density and hence vary for samples with different doping concentrations. Increase in the peak of Raman shift (frequency) and width of LPP mode, signifies increase in carrier density. For low carrier density, the character of LPP mode is phonon like due to reduced plasmon-phonon coupling. However, with increasing carrier density the LPP peak shifts towards higher frequency while the intensity reduces and eventually the peak broadens due to increase in the coupling strength (see figure 3). Cheng et al [18] have shown, in case of ZnO NRs, the LPP phonon peak broadening and shifting towards higher frequency with an increase in carrier concentration, which is consistent with our observations. Ding et al [19] and Jeganathan et al [20] have also reported similar behavior of LPP mode in Al-doped ZnO and Si-doped GaN, respectively.

The peak position and FWHM of SO and LPP Raman modes is tabulated in table 1, where we note that the linewidth of LPP mode is strongly influenced by Mg concentration in the films. The deconvoluted Raman spectra reveal that the FWHMs of SO mode have a similar value of \( \approx 20 \text{ cm}^{-1} \) for all the samples under consideration (see figure 2 (b)). We find that FWHM of LPP mode is significantly high (\( \approx 30 \text{ cm}^{-1} \)) for undoped sample A in comparison to the Mg doped ones, where the FWHM values are 17.0, 13.0 and 9.7 cm\(^{-1} \) for samples B, C and D, respectively (see figure 2(b)). The FWHM of \( A_1(LO) \) mode of high resistive GaN film is \( \approx 9 \text{ cm}^{-1} \) (data not shown here) which suggest that peak observed here for samples A, B and C are LPP coupled mode but for sample D the LPP coupled mode may have transformed into \( A_1(LO) \) mode. This observation is consistent with our XPS data as sample D has hole carriers where plasmon phonon coupling is difficult due to absence of plasma. Also to make sure that the changes in the FWHM of LPP mode are not due to any structural changes in the NRs samples, we carried out \( \omega\)-scan using HR-XRD studies, whose width characterizes the crystalline quality of the films. The FWHM of the (0002) planes as obtained from \( \omega\)-scan are noted as 2.94 deg.
0.70 deg, 0.93 deg and 0.99 deg for samples A, B, C and D respectively (see figure 4). Thus, there is no direct correlation between crystal quality and peak broadening of the LPP mode. Thus, the changes in the width of line shapes of Raman spectra becomes very significant and can be used as a non-contact tool for the quantification of carrier concentration. We further fitted the deconvoluted LPP mode with equation (1), and the fitted plot is shown as solid lines with olive shade in figure 2(b). The obtained values of \( n_e, \gamma \) and \( \Gamma \) from the fitted curve are also tabulated in table 1. Our estimate to the background carrier density for undoped GaN NRs sample (A) is \( 1.5 \times 10^{17} \text{ cm}^{-3} \), which is of the same order of carrier density that is commonly observed in MBE grown GaN samples [17]. For lightly Mg doped samples B and C the background n-type carrier densities are estimated to the order of \( 10^{15} \text{ cm}^{-3} \), suggesting that Mg incorporation has compensated the background carrier densities by two orders of magnitude. It is noteworthy to mention here that sample D is p-type thus, extracting the carrier density using method discussed above is not meaningful.

The \( E_2(\text{high}) \) mode, being non-polar in nature, can be used as a measure of the inherent strain of the material. The FWHM of this mode reflects defect incorporation in the film, since strain gradient or phonon-defect scattering can lead to the broadening of this mode. We find a small change in the position of \( E_2(\text{high}) \) peak (from 567.35 to 567.39 cm\(^{-1}\)) which suggests that a very small macroscopic strain is being generated in the NRs with Mg incorporation. We also find that with the increase in Mg-flux, FWHM of \( E_2(\text{high}) \) peak increases,

![Figure 3](image-url)  
Figure 3. Graphical representation of equation (1) with varying carrier concentration (\( n \)). The values of \( \chi \) are in \( \text{cm}^{-3} \) unit. Here the values of \( C, \gamma, \Gamma, m^*, \omega_{\text{TO}} \) and \( \omega_{\text{LO}} \) are taken as 0.48 [21], \( 8.5 \times 10^{13} \text{ s}^{-1} \), \( 1.35 \times 10^{15} \text{ s}^{-1} \), 0.18 \( m_e \) [22], 5.4 [23], 531.8 [14] and 734.0 [14], respectively.

| Sample name | Mg:Ga | Peak position (cm\(^{-1}\)) | FWHM (cm\(^{-1}\)) | \( n_e \) (cm\(^{-3}\)) | \( \gamma \) (THz) | \( \Gamma \) (THz) |
|-------------|-------|-----------------------------|---------------------|-------------------------|-----------------|-----------------|
| A           | 0.0000 | 737.3                       | 30.9                | \( 1.5 \times 10^{17} \) | 300             | 0.10            |
| B           | 0.0082 | 738.8                       | 17.0                | \( 4.5 \times 10^{15} \) | 9               | 0.40            |
| C           | 0.0113 | 738.3                       | 13.0                | \( 3.6 \times 10^{15} \) | 1               | 0.40            |
| D           | 0.0162 | 739.3                       | 9.7                 | —                       | —               | —               |

![Figure 4](image-url)  
Figure 4. (a)–(d) \( \omega \)-scans of samples A, B, C and D, respectively.
which can be attributed to the generation of different kinds of point defects in the samples, depending on the concentration of Mg incorporation [24]. The origin of the native $n$-type behavior of GaN is still ambiguous in the literature. Defects such as N vacancies ($V_N$) [25] and Oxygen substitution ($O_{GN}$) [26] are reported as the major source of such auto-doping in GaN. Theoretical calculations based on first-principles method further suggest that Oxygen substitution in the form of $V_{GN}O_N$ is energetically more favorable [27]. Our previous work [28] further suggests that defect formation energy of the $V_N$ at the surface is much less than in the bulk and thus $V_N$ is a major point defect in nanostructured GaN due to its’ higher surface to volume ratio [28]. Luminescence spectra recorded for sample A (undoped) shows a near band edge (NBE) peak at 3.4 eV and a broad YL at 2.20 eV (see figure 5). However, recent theoretical calculations show that $V_N$ and carbon related defects may give rise to energy states in the bandgap that is responsible for the yellow luminescence (YL) observed in PL spectra of n-GaN, while $V_{GN}O_N$ does not [29]. Thus, n-type and YL together suggest that $V_N$ is the dominant defect type in this case. This speculation is further backed by the luminescence spectra obtained from sample B and C (moderately doped ones), wherein a green luminescence (GL) peak is observed at $\approx$2.54 eV along with NBE and a donor acceptor pair (DAP) transition at $\approx$3.2 eV (see figure 5). The 3.2 eV luminescence peak is the consequence of the formation of the substitutional Mg in GaN ($Mg_{Ga}$). Reshshikov et al [30] studied the defects in Mg doped GaN and suggested that most energetically favorable point defect is $V_N$, which gives rise to green luminescence, while defect complex $Mg_{Ga}$ results in red bands [30]. Our experimental PL data shows only GL band and a DAP transition at 3.2 eV (sample B and C), thus confirming the formation of isolated $V_N$ and $Mg_{Ga}$ in Mg doped GaN NRs. Each isolated $V_N$ results in one electron per vacancy, while $Mg_{Ga}$ may result in a free hole. Thus, formation of individual $V_N$ and $Mg_{Ga}$ will not result in any change in carrier concentration. SIMS measurements [12] on these samples reveal Mg concentrations of $4.9 \times 10^{19}, 6.0 \times 10^{19}$ and $2.9 \times 10^{20}$ atoms cm$^{-3}$. The reduction in background carrier density ($n_e$) with increase in Mg concentration suggests that $V_N$ concentration is less than $4.9 \times 10^{19}$ cm$^{-3}$ in these samples. The compensation effect observed here is due to formation of isolated $Mg_{Ga}$ which compensates the native n-type character caused by formation of isolated $V_N$ in unintentionally n-doped GaN. For sample D blue luminescence peak centered at $\approx$2.87 eV is observed with band edge emission, which suggest that self compensating $Mg_{Ga} + Mg$ defect complexes are generated in the sample [31].

In summary, we have grown Mg doped GaN NRs on Si (111) surface and studied the native charge compensation effect in the same using optical and x-ray photoelectron spectroscopies. Two order magnitude of native charge compensation was deduced upon Mg-doping with a concentration of $10^{19}$–$10^{20}$ atoms cm$^{-3}$ by analysing the line shape profile of the longitudinal plasmon-phonon coupled Raman mode. Thus the line shape of the longitudinal plasmon–phonon coupled Raman mode could be a contactless method in determining the charge carrier density and the dopant induced compensation in nanostructured materials.

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References

[1] Ihn S-G, Song J-I, Kim Y-H and Lee J Y 2006 Appl. Phys. Lett. 89 053106
[2] Li L, Guimard D, Rajesh M and Arakawa Y 2008 Appl. Phys. Lett. 92 263105
[3] Cerutti J, Ristic J, Fernández-Garrido S, Calleja E, Tranpert A, Ploog K, Lazic S and Calleja J 2006 Appl. Phys. Lett. 88 213114
[4] Mårtensson T, Svensson C P T, Wacaser B A, Larsson M W, Seifert W, Deppert K, Gustafsson A, Wallenberg L R and Samuelson L 2004 Nano Lett. 4 1987
[5] Glas F 2006 Phys. Rev. B 74 121302
[6] Verheijen M A, Immink G, de Smet T, Borgström M T and Bakkers E P 2006 J. Am. Chem. Soc. 128 1353
[7] Robins L H, Horneber E, Sanford N A, Bertness K A, Brubaker M and Schlager J 2016 J. Appl. Phys. 120 124313
[8] Kang Li, Guimard D, Rajesh M and Arakawa Y 2008 Appl. Phys. Lett. 92 263105
[9] Cerutti L, Ristić J, Fernández-Garrido S, Calleja E, Tranpert A, Ploog K, Lazic S and Calleja J 2006 Appl. Phys. Lett. 88 213114
[10] Mårtensson T, Svensson C P T, Wacaser B A, Larsson M W, Seifert W, Deppert K, Gustafsson A, Wallenberg L R and Samuelson L 2004 Nano Lett. 4 1987
[11] Glas F 2006 Phys. Rev. B 74 121302
[12] Verheijen M A, Immink G, de Smet T, Borgström M T and Bakkers E P 2006 J. Am. Chem. Soc. 128 1353
[13] Robins L H, Horneber E, Sanford N A, Bertness K A, Brubaker M and Schlager J 2016 J. Appl. Phys. 120 124313
[14] Davydov V Y, Kitaev Y E, Goncharuk I, Smirnov A, Graul J, Semchinova O, Ullmann D, Smirnov M, Mirgorodsky A and Evarestov R 1998 Phys. Rev. B 58 12499
[15] Aruhatu T, Sota T, Suzuki K and Nakamura S 1995 J. Phys. Condens. Matter 7 L129
[16] Siegle H, Kaczmarszyk G, Filippidou L, Livinchuk A, Hoffmann A and Thomesen C 1997 Phys. Rev. B 55 7000
[17] Robins L H, Horneber E, Sanford N A, Bertness K A, Brubaker M and Schlager J 2016 J. Appl. Phys. 120 124313
[18] Cheng A-I, Tseng Y, Xu H, Alur S, Wang Y, Park M, Wu T-H, Shannon C, Kim D-J and Wang D 2009 J. Appl. Phys. 105 075301
[19] Ding K, Hu Q, Lin W, Huang J and Huang F 2012 Appl. Phys. Lett. 101 031908
[20] Jegnathan K, Debnath R, Meijers R, Stoica T, Calarco R, Grützmacher D and Lüth H 2009 J. Appl. Phys. 105 123707
[21] Harima H 2002 J. Phys. Condens. Matter 14 4967
[22] Suzuki M, Uenoayama T and Yamanaka S 1995 Phys. Rev. B 52 8132
[23] Melentev G, Yaichnikov D, Shalygin V, Vinnichenko M Y, Vorobjev L, Firsov D, Riutinanen L and Suihkonen S 2016 J. Phys. Conf. Ser. 690 (Bristol: IOP Publishing) p 012005
[24] Kirste R et al 2013 J. Appl. Phys. 113 103504
[25] Boguslawski P, Briggs E L and Bernholc J 1995 Phys. Rev. B 51 17255
[26] Van De Walle C G and Neugebauer J 2004 J. Appl. Phys. 95 3851
[27] Neugebauer J and Van De Walle C G 1996 Appl. Phys. Lett. 69 503
[28] Nayak S, Naik M H, Jain M, Waghamare U and Shivaprasad S 2017 arXiv:1710.05670
[29] Reshchikov M, Albarakati N, Monavarian M, Avrutin V and Morkoc H 2018 J. Appl. Phys. 123 165120
[30] Reshchikov M A, Demchenko D, McNamara J, Fernández-Garrido S and Calarco R 2014 Phys. Rev. B 90 035207
[31] Nayak S, Gupta M, Waghamare U V and Shivaprasad S 2019 Phys. Rev. Applied 11 014027