Optical characterization of magnesium incorporation in p-GaN layers for core–shell nanorod light-emitting diodes

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Abstract

III-nitride nanostructures are of interest for a new generation of light-emitting diodes (LEDs). However, the characterization of doping incorporation in nanorod (NR) structures, which is essential for creating the p-n junction diodes, is extremely challenging. This is because the established electrical measurement techniques (such as capacitance–voltage or Hall-effect methods) require a simple sample geometry and reliable ohmic contacts, both of which are difficult to achieve in nanoscale devices. The need for homogenous, conformal n-type or p-type layers in core–shell nanostructures magnifies these challenges. Consequently, we demonstrate how a combination of non-contact methods (micro-photoluminescence, micro-Raman and cathodoluminescence), as well as electron-beam-induced-current, can be used to analyze the uniformity of magnesium incorporation in core–shell NRs and make a first estimate of doping levels by the evolution of band transitions, strain and current mapping. These techniques have been used to optimize the growth of core–shell nanostructures for electrical carrier injection, a significant milestone for their use in LEDs.

Keywords: p-GaN, doping, core–shell, nanorod, cathodoluminescence, EBIC

(Some figures may appear in colour only in the online journal)
contacts. In planar layers, the doping density and the effect of Mg activation can be measured using standard electrical methods. However, in column-shaped nanostructures the three-dimensionality of the columns, the different facet geometry, and connection of the NRs require the development of alternative characterization techniques.

The incorporation of Mg atoms during metal organic vapor phase epitaxial (MOVPE) growth from the bis(cyclopentadienyl)-magnesium (Cp₂Mg) precursor introduces characteristic emission peaks observed in micro-pho-
toluminescence (PL) and cathodoluminescence (CL) spectra, which can be used as an indication of Mg doping. The origins of the main features are summarized in the following:

1. A main luminescence peak at 3.27 eV has been commonly attributed to a donor–acceptor-pair (DAP) transition [7] between the Mg acceptor level and a hydrogen-related donor level [8–10]. Note, the presence of hydrogen in MOVPE growth passivates the Mg and increases the p-GaN shell resistivity, requiring a thermal treatment to break the hydrogen bonds and activate the Mg dopant, providing free holes [11].

2. At least one further luminescence peak has been observed at ~3.15 eV in highly Mg-doped GaN, and has been attributed in the literature to a Mg-related DAP type recombination via a perturbed state near the Mg acceptor level [10].

3. The formation of a 2.80–2.95 eV blue luminescence band (BL) was observed in optical measurements for even higher doping, at Mg atomic concentrations greater than 2 \times 10^{19} \text{cm}^{-3}. This doping level triggers electrical self-compensation [12–14], which is accompanied by increased electrical resistivity. Increased tensile strain in the crystal lattice [15] has also been correlated with self-compensation. The BL is possibly related to an increase in the probability that transitions occur between the Mg acceptor level and a deep-donor-level. The deep donor level is possibly related to a nitrogen vacancy V_N [12, 13] or a hydrogenated Mg–V_N–H complex [9, 16], though a different view is taken in [17] which proposed the Mg–H complex is responsible for the 3.27 eV DAP emission, with the BL emission being attributed to the isolated and electrically active Mg atom.

This paper shows how a combination of optical methods can provide a contactless procedure for obtaining information about Mg incorporation in p-type GaN nanostructures that would be impossible to obtain by conventional electrical methods. In addition, we confirm the presence of a uniform p-n junction through electron-beam-induced-current (EBIC) measurements of cross-sectioned NRs.

2. Experimental methods

Magnesium-doped p-GaN shells were grown on n-type GaN NR cores, formed by etching and regrowth, by MOVPE at different growth temperatures, with different Mg precursor flows and annealing treatments to activate the hole carriers. The uniformity and activation of Mg impurities in the p-GaN shells were analyzed by scanning electron microscopy (SEM), \( \mu \text{PL} \), CL and Raman spectroscopy and EBIC. These methods were chosen because they are non-contact, non-destructive and reveal the impact of Mg-doping on surface morphology [18], optical transitions [19–21] and changes in strain with Mg incorporation [15, 22]. The characterization was performed at room temperature and the spectral changes introduced by Mg doping can be identified and used to guide the design of the p-shell, even though the signature Mg peaks are harder to resolve than at low temperature. Normalized intensities are plotted to compensate the changing focus on different NR samples, which affects the relative signal intensities.

P-N core–shell GaN NRs were obtained by lateral regrowth on plasma-etched GaN cores, as shown in the SEM images in figure 1. The array of GaN cores was obtained by the deposition of a nickel nano-dot metal etch mask with 2 \( \mu \text{m} \) pitch periodicity on planar GaN followed by Cl₂–Ar etching [23]. Two sample sets were prepared from GaN layers on two different substrates: a 2 \( \mu \text{m} \) thick undoped GaN-on-Si substrate (with an intermediate AlN buffer layer), and a 5 \( \mu \text{m} \) n-doped GaN film on sapphire. The GaN-on-Si substrate was etched completely through the GaN layer to expose the underlying Si, whilst the GaN-on-sapphire substrate was etched only to a depth of 3 \( \mu \text{m} \) to retain a conductive n-GaN layer of 2 \( \mu \text{m} \) thickness below the NRs. To promote regrowth on the NR \( \{10 \overline{1} 0\} \) m-plane sidewalls, the Si substrate and the remaining GaN planar layer on sapphire were protected by passivation. The passivation was achieved by the formation of SiNx on the exposed Si during \textit{in situ} nitridation, or, in the case of the samples on sapphire substrates, by spin-coating hydrogen silsesquioxane (HSQ) on the remaining planar GaN before regrowth. During regrowth the passivation maintains highly uniform m-plane facets for the p-GaN shell growth [24]. A sapphire substrate provides a platform for thicker GaN layers without introducing AlxGa1-xN strain relief layers as required for GaN growth on Si substrates. This allowed taller GaN cores to be etched from a uniform epitaxial layer, thereby enabling assessment of Mg incorporation into the layers grown on the sidewalls of high-aspect-ratio NR arrays.

An initial set of growth temperatures was tested on the GaN-on-Si NRs samples, with 10 min of p-GaN growth and a fixed precursor flow of 0.44 \( \mu \text{mol min}^{-1} \text{Cp}_2\text{Mg}. This will be referred to as a \textit{medium} doping flow. A high V/III ratio (2780) was expected to provide high Mg incorporation without occurrence of self-compensation [25]. The lack or minimal effect of self-compensation was verified by optical means and the presence or absence of the BL emission [12]. Three different annealing temperatures of 620 °C, 720 °C and 820 °C were applied for 20 min under nitrogen gas to decompose the Mg–H or Mg–V_N–H complexes.

A further set of samples on Si and sapphire substrates was used to study the effect of different doping flow rates at a constant growth temperature of 800 °C. The \textit{Cp}_2\text{Mg} dopant precursor flow rates were adjusted between: 0.30 \( \mu \text{mol min}^{-1} \) (low), 0.44 \( \mu \text{mol min}^{-1} \) (medium), and 0.71 \( \mu \text{mol min}^{-1} \) (high). These flow rates were equivalent to \textit{Cp}_2\text{Mg}/TMGa ratios of 0.98%, 1.43% and 2.26%, and were used for growing
p-type shells on NRs formed on both Si and sapphire substrates. The sapphire substrate samples were grown at 800 °C using the three different flows for 20 min, to provide a longer growth time on the higher-aspect-ratio NRs. Also an annealing time of 10 min was used for the sapphire-based samples to reduce the risk of GaN dissociation on the thinner p-GaN shell on these structures.

Micro-PL characterization was performed with a He–Cd 325 nm laser excitation source at 0.135 mW power output and a 2400 lines mm⁻¹ diffraction grating in order to obtain a good signal to noise ratio. A 40× magnification, 0.50 numerical aperture (NA) objective produced a spot size of ~0.8 µm, small enough to probe single NRs on a 2 µm pitch. Measurements were repeated on several NRs to account for NR-to-NR variation. For even greater spatial resolution, CL maps were obtained on a subset of samples, using an electron beam with a low energy of 2 keV as a compromise between a good beam focus at relatively large working distance (8 mm) and spatial resolution. CL scans were performed on the top, middle, and bottom sections of individual and neighboring NRs to test for position-dependent variations in the spectra ascribable to variations in Mg incorporation.

Raman spectroscopy was used to detect and map atomic displacements introduced by the Mg impurities, by probing the changes in the \( E_2^H \) and \( A_1^{LO} \) Raman peaks. Specifically, shifts in the \( E_2^H \) peak can be associated with strain variation, which can be caused by the formation of compensating defects that occur during Mg doping [22].

To probe the atomic displacements, a high-resolution confocal Raman spectrometer (Renishaw inVia) with a 532 nm laser source, 3000 lines mm⁻¹ grating and 150×, 0.95 NA objective was used. The laser power was 10 mW, the lateral spatial resolution was 0.3 µm and the measurement resolution of the spectral shift was 0.01 cm⁻¹. Raman spectroscopy was carried out both on standing NR arrays on GaN/sapphire and on NRs mechanically removed from the GaN and dispersed horizontally on a clean sapphire substrate to eliminate the influence of the underlying GaN. For NRs grown on Si, the Si and AlN rod pedestals remained attached to the GaN NRs, and hindered reliable determination of the position and width of the GaN \( E_2^H \) peak. Therefore only the core–shell NRs grown on sapphire substrates are discussed. Raman maps were obtained by scanning with a 0.1 µm step size across mechanically detached NRs to study Mg or impurity distribution in the p-shell.

EBIC measurements were used to assess the electrical properties of these nano-structures to overcome the difficulty in forming ohmic contacts on core–shell NRs. The EBIC method provides imaging of the p–n junction. The focused electron beam creates electron–hole pairs by local excitation of the p–n junction on the individual NRs. The application of a voltage drop by nanoprobe between the GaN substrate (n-contact) and different regions of the NR p–n junction provides information on the junction depletion width, uniformity of dopants, the local bias, carrier concentrations and local junction defects. An overview of EBIC on p–n junctions can be found in [26].
3. Results

3.1. Micro-PL and CL

Micro-PL (room temperature) spectra of the p-n junction core–shell NRs grown at different temperatures on cores etched from a GaN-on-Si substrate are compared in figure 2(a). The spectra show very similar peaks for all the growth temperatures before an annealing step, except for the sample grown at 1000 °C, for which the relevant spectrum indicates that Mg incorporation was less effective, probably due to p-GaN dissociation at such a high growth temperature. The NR shape and diameter variability was quantified statistically by image processing [27], and as a result further p-GaN growths were carried out at 800 °C, which provided the more regular m-plane p-GaN facets and less variable PL spectra.

The room temperature near-band-edge (NBE) emission at 3.41 eV from the samples appears as a slight shoulder in the micro PL but is more clearly resolved in the CL measurements of figure 3. Instead, in the micro PL, a peak at 3.35 eV dominates the high-energy side of the spectra for all regrown samples. There are alternative proposals in the literature for the origin of this peak, for example it being related to stacking faults [28] or being due to H2 in the reactor [29]. However, experimental data (not shown) comparing PL data at different stages of processing show that this peak is introduced during the etching of the NRs from the planar film and becomes dominant after GaN regrowth prior to the growth of the p-type shell. Therefore, we tentatively attribute it to defect states introduced during the etching, and turn our attention to the peaks more clearly identified as being due to Mg doping.

The peak at 3.27 eV in figure 2(a) is widely identified in planar p-GaN with a shallow DAP (DAP1), a radiative transition related to Mg-doping. Also, a DAP-type emission has been previously observed at 3.27 eV in m-plane GaN films [30] and in arrays of Mg-doped nanowires, in both low and room temperature PL [31, 32].

In our samples the energy of the DAP1 peak did not change significantly with growth temperature or after annealing. However, the ratio of the intensity of the DAP1 to the intensity of the 3.35 eV peak was reduced following annealing at 720 °C in N2 ambient for 20 min, as shown in figure 2(b), and to a greater degree for the lower growth temperatures. A reduction of the DAP1 intensity is consistent with the breaking of Mg–H bonds formed during growth, i.e. the Mg acceptor had been activated [33].

A peak at 3.24 eV can just be resolved in the micro-PL below the 3.27 eV peak. In the literature a peak at this energy has been related to a deeper Mg ground state, ~30 meV lower than the transient shallow Mg acceptor (i.e. DAP1) [34]. This energy value may relate to a DAP pair transition (DAP3) when Mg atom impurities are above $5 \times 10^{18}$ cm$^{-3}$ [20].

Therefore, the presence and intensity of the 3.27, 3.24 and 3.16 eV peaks, collectively forming a broad DAP band, provide a potentially useful signature for the presence of Mg incorporation in p-GaN core–shell NRs.

Phonon-assisted transitions, caused by the coupling of phonons (longitudinal optical phonons) to the DAP1, have been shown to introduce additional spectral lines at regular intervals, in both NRs and planar layers, while maintaining the shape of the original DAP peak [35–38]. Due to the irregular scattering geometry of the NRs, a mixing of phonon modes is possible resulting in quasi-LO modes with spectral positions shifted compared to literature values [39]. Furthermore, using room-temperature spectra, only tentative values can be associated with the phonon-assisted transitions, which is not in the scope of the present work.
A set of samples was analyzed by spectrally-resolved CL using a 2keV electron beam to investigate the spatial distribution of Mg impurities. The samples were grown under three different Cp₂Mg precursor flows for 10 min at a growth temperature of 800 °C and subsequently annealed at 720 °C. The emission spectrum excited by the 2keV electron beam is highly sensitive to the level of Mg doping, as shown in figure 3(a).
The spectra in figure 3(a) reveal a broadening of the CL that grows with increasing Cp2Mg flow due to the emergence of Mg acceptor-related emission peaks in the 3.2–3.3 eV photon energy range. At the medium Mg doping level, the 3.24–3.27 eV DAP signature appears as a clearly pronounced shoulder in the CL spectrum. Therefore, by focusing on an emission energy of 3.27 eV, CL maps in figure 3(d) reveal the uniformity of Mg incorporation across the NR. The DAP emission is visible from the entire m-plane and much of the semi-polar planes. Furthermore, it becomes dominant in the sample grown at the highest Cp2Mg flow rate, indicating the presence of a significantly higher density of Mg acceptors in this sample. However, as can be seen in figure 3(e), the emission is non-uniform, coming predominantly from the lower part of the semipolar facets and very localized regions of the m-planes. A similar reduction in DAP emission intensity at high Mg doping for the NR pyramid and base regions was recently shown in [40].

The CL excited by the 2 keV electron beam originated from a depth of 100 nm, as estimated from Monte-Carlo Casino simulations, which was sufficient to probe partially the underlying NID GaN. The DAP to NBE signal ratio reduced for 3 keV excitation, as the penetration depth was increased. As the accelerating energy was increased to 5–7 keV, the NPs showed uniform NBE emission from the entire m-plane area. This demonstrates that the DAP emission comes from the Mg doped shell and that low accelerating voltage CL maps provide an effective measure of the Mg doping uniformity.

A set of samples on sapphire substrates with higher aspect ratio NRs (3 μm tall compared with 1.5 μm for those on silicon) using the same growth parameters were studied, and are shown in figure 4. To maintain electrical isolation of the continuous n-GaN layer beneath the etched NRs, the base of the columns was passivated with HSQ prior to crystal growth. This is visible as a dark layer at the bottom of the NRs in figures 4(a) and (d).

Panchromatic intensity CL maps (integrated over all emission wavelengths) of a group of tall core–shell NRs are compared in figures 4(b) and (e) for the low and high Cp2Mg flows. The corresponding CL spectra in figure 4(c) are plotted on a log scale for better visibility. In contrast to the shorter NRs grown on silicon, the DAP1 transition appears as a weak shoulder relative to the 3.35 eV peak.

The lack of emission from the vertically aligned apices could indicate a possible higher concentration of local non-radiative recombination complexes or defects formed in these regions, or could be an artifact due to the distribution of light in the guided modes of the NRs and its effect on the light extraction.

3.2. Raman spectroscopy

Raman spectroscopy can be applied to p-GaN layers to study the shift of the \( E_{2}^{1} \) peak position [39] corresponding to the strain introduced by Mg impurity atoms in the GaN lattice. Unstrained GaN films have Raman \( E_{2}^{1} \) mode frequency values of \( 567.6–568 \) cm\(^{-1} \) [39]. In thin GaN-on-sapphire layers grown along the c-direction, the compressive strain results in \( E_{2}^{1} \) values of \( \approx 570 \) cm\(^{-1} \), while for GaN layers on Si substrates, with an AlN buffer layer, the \( E_{2}^{1} \) has a position of \( \approx 568 \) cm\(^{-1} \), indicating a material similar to unstrained GaN [41].

The p-GaN shells obtained for the tall NRs on the sapphire substrate have, on average, a 50 nm sidewall thickness, covering a strain-relaxed GaN core of 720 nm diameter [42]. Because of the relative thickness ratio of p-GaN to GaN, changes in the \( E_{2}^{1} \) peak position were expected to be small, requiring a high resolution detection system. NRs were mechanically removed from the substrate and placed on a clean sapphire substrate to improve the signal-to-noise ratio and to separate the NRs from any underlying GaN. The NR Raman spectra can be influenced by small changes in the geometry of the NRs, because the observed modes can change with the incident angle of the laser beam to the NR surfaces. Therefore, a unique alignment of the dispersed NRs was considered and verified with the optical objective. This alignment is equivalent to using the \( y(x,-y) \) Raman selection rule, with the incident laser beam perpendicular to the NR’s \( \{10-10\} \) m-plane. In this configuration the Raman-active phonon modes are restricted to the \( E_{2}^{1} \), the \( A_{1}^{\text{TO}} \) and the \( E_{1}^{\text{TO}} \) modes, as seen in figure 5. Spectra of individual dispersed NRs with identical orientation were collected and averaged to determine the peak position of \( E_{1}^{\text{TO}} \) for differently doped NRs.

The inset in figure 5(a) shows the Raman \( E_{1}^{\text{TO}} \) peak shifting towards tensile strain, from 567.56 cm\(^{-1} \) for NID GaN core–shell structures, to 567.51 cm\(^{-1} \) for high Mg flow (table 1). The NR shell thickness was determined from planar SEM images using image processing software [27]. Kirste et al proposed for planar layers that a compensating Mg–V\(_{N} \) complex occurs during Mg doping to cause the shift towards tensile strain [22]. Another known indication of active p-GaN is the presence of the Raman 657 cm\(^{-1} \) peak [43]. However, for effective hole densities in the range of \( 1 \times 10^{17} \) cm\(^{-3} \), such a peak is difficult to resolve [18] and was not observed in the sample sets described here.

Figure 5(b) shows Raman spectra taken from standing NRs from GaN-on-sapphire, in the \( z(x,-y) \) Raman configuration. The same small \( E_{2}^{1} \) peak shift was observed on the NR array as with the dispersed NRs. The standing NRs may provide information about doping from the \( A_{1}^{\text{LO}} \) peak, as shown in the inset of figure 5(b). In the case of n-type GaN, the doping levels can be estimated from the shift of the \( A_{1}^{\text{LO}} \) peak, caused by longitudinal optical phonon-plasmon coupling (LOPC) [39]. However, the effect of LOPC is less clear in the case of p-type GaN.

The inset in figure 5(b) shows that the broadening of the \( A_{1}^{\text{LO}} \) peak correlates with the introduction of Mg atoms into the crystal lattice. Even if the concentration of holes in the thin p-GaN sidewall was not sufficient to shift the \( A_{1}^{\text{LO}} \) peak, its width has increased with higher Mg flows, in agreement with [44] in which it was argued that the \( A_{1}^{\text{LO}} \) phonon does not change its coupled position for hole carriers below \( 10^{18} \) cm\(^{-3} \).
However, for hole concentrations above $1 \times 10^{18}$ cm$^{-3}$, the $A_{1}^{(LO)}$ peak position can shift systematically over values in the range of 732–740 cm$^{-1}$ [45].

The dopant or defect distribution in the p-GaN layer may affect the current spreading of the doped p-shell. The CL analysis presented in section 3.1 revealed that the DAP1 emission became markedly less uniform for higher flow rates of the Mg precursor. High-resolution Raman 2D mapping in $y(x, -)\gamma$ mode was used to investigate local variations in p-shell strain from individual NRs as a function of Cp2Mg precursor flow. Figure 6 shows Raman $E_{2}^{H}$ peak maps from dispersed NRs collected with a spatial resolution of 0.1 µm. The signal was curve fitted and filtered to a threshold level of $E_{2}^{H}$ peak intensity, considered to represent the surface profile of each NR.

For the structure with an unintentionally doped GaN shell in figure 6(a) the $E_{2}^{H}$ peak position does not change from tip to base or from side to side, as the color is uniform across the sample. The dark blue spots indicate local variations in the regrown NRs, potentially due to the presence of extended defects. In figure 6(b) the color map, corresponding to the $E_{2}^{H}$ peak position, shows no significant changes along the length of the $m$-plane of the medium-doped NRs, with only a very gradual change in strain towards the tip. This correlates with the uniform CL intensities observed earlier on medium-doped samples. For the case of high doping in figure 6(c), a less uniform color map, corresponding to variation in the $E_{2}^{H}$ value, is observed, indicating the tip and bottom of the NR show change towards tensile strain. The spectral range of all color maps was identical. On average, the value of the $E_{2}^{H}$ peak position was quantified to be 0.1 cm$^{-1}$ wavenumbers lower in the highly-doped sample; a measureable difference.

### Table 1. Variation of NR thickness and values of $E_{2}^{H}$ Raman mode wave number with doping.

| Sample                  | Diameter (nm) | $E_{2}^{H}$ position for an individual NR (cm$^{-1}$) | $E_{2}^{H}$ position of NRs within an array (cm$^{-1}$) |
|-------------------------|---------------|-----------------------------------------------------|------------------------------------------------------|
| GaN core only           | 724 (20)      | 567.563 (0.022)                                      | 567.563 (0.026)                                      |
| Low p-doped shell       | 773 (39)      | 567.567 (0.012)                                      | 567.566 (0.014)                                      |
| Medium p-doped shell    | 744 (20)      | 567.524 (0.027)                                      | 567.523 (0.030)                                      |
| High p-doped shell      | 763 (27)      | 567.514 (0.038)                                      | 567.515 (0.044)                                      |

### 3.3. Electron-beam-induced-current (EBIC)

The EBIC method can be applied to nanostructures to reveal the local electric fields and effects of local variations in doping density on the recombination of active carriers. In our sample configuration, the regrown GaN NRs with a p-GaN layer (p-side) were separated by passivation from a common GaN n-contact, producing a p-n junction perpendicular to the plane of the growth substrate. The p-n junction in the samples is perceptible at 0 V bias, and the width of the depletion area increases when reverse bias is applied, or decreases for forward bias. The direct measurement of EBIC current between the n-layer and individual NR p-GaN shell resulted in poor current spreading at the contact point of the tungsten probe, likely due to the very thin p-GaN shell (60–80 nm) and the potential barrier between the probe and the GaN. Thus, a thicker medium-doped p-GaN shell (~200 nm sidewall) sample was grown, and a transparent indium tin oxide (ITO) ohmic contact was deposited conformal to the NRs. The NRs were cross-sectioned to expose the p-n junction and to allow an EBIC profile to be obtained, to create p-n junction contrast maps as shown in figure 7. In figures 7(a) and (b) the
different layers can be identified from the overlap of the SEM SE and EBIC images. The false color EBIC map (figure 7(b)) proves that most of the junction extends in the p-GaN layer. The width of the $p$-$n$ junction was measured as 150–200 nm at a $U_{\text{bias}}$ of 0 V and an electron beam energy of 2 keV. The CL peak corresponding to the DAP2 transition can be visualized being conformal to the p-GaN shell profile. Figure 7(c) combines CL and SE images and indicates the active Mg species, providing minority carriers, can be associated with the DAP2 transition, or it may be a direct correlation with the atomic concentration incorporated at the cross-sectioned NR base. Although the side and top profile of CL emission show some variation in the distribution of DAP2 along the NR, using a conductive oxide to improve current spreading results in a continuous $p$-$n$ junction section. This indicates a smooth and defect free junction with uniform depletion width can be achieved on the core–shell NRs with p-GaN and ITO layers.

Using the average value of the $p$-$n$ junction width as measured from the SEM and EBIC signals measured at 2 keV e-beam energy, the active hole carrier doping level in medium-doped NRs forming the asymmetric $p$-$n$ junction was estimated to be between $8 \times 10^{16}$–$1.4 \times 10^{17}$ cm$^{-3}$. This estimate was obtained by measuring the depletion width and the built-in potential [26, 46, 47] and knowledge of the electron
carrier concentration for the GaN templates \(1 \times 10^{19}\) cm\(^{-3}\). In fact, this is a lower estimate since the effect of the generation region cannot be neglected even at 2 keV, the minimum energy required for proper focusing of the e-beam at the working distance required for the microprobes. As specified in [12, 47] only a small percentage of the Mg atoms can provide active holes. Therefore, a mobile carrier concentration in the range near \(1 \times 10^{17}\) holes cm\(^{-3}\) estimated from EBIC agrees with the initial estimates of Mg atomic concentrations of \(5-7 \times 10^{18}\) cm\(^{-3}\) derived from the PL and CL measurements.

4. Discussion

The spectra from the room temperature \(\mu\)PL, CL and Raman spectroscopy of the sample sets show a consistent qualitative dependence on the growth temperature, Mg precursor flows and annealing treatment. A growth temperature of 800 °C was found to provide good growth rate and sidewall uniformity. Subsequent annealing at 720 °C then reduced the DAP transitions.

The Mg dopant introduced a broad sub-band-edge emission band; optical DAP transitions between 3.15–3.27 eV. Based on the literature and experimental observations, features in this band can be attributed to DAP transitions between the Mg acceptor and a hydrogen-related donor level. Deeper transitions between the Mg level and a nitrogen vacancy \(V_N\) or a complex involving \(V_N\) are also possible. For a Mg atomic concentration below \(1 \times 10^{18}\) cm\(^{-3}\), it was previously reported that only the DAP1 transition is present [10]. The observation of additional lines is an indication that the p-shell in our samples has a higher Mg doping concentration. The peaks at 3.27, 3.24 eV and the lack of a dominant blue band emission indicate a likely Mg atomic concentration below \(~5-7 \times 10^{18}\) cm\(^{-3}\). In order to determine an estimate for the active hole concentration for this concentration of Mg atoms, we cross reference with [14], which examines the relationship between active holes and Mg atoms. Therefore, we deduce a hole concentration or ionized acceptor concentration in our samples of \(0.5-2 \times 10^{17}\) cm\(^{-3}\).

Tall NRs in figures 4(b) and (e) showed uniform emission along the \(m\)-plane sidewall compared to the short NRs, even with a high doping level. The uniformity may be attributed to the increase in GaN surface area for the tall NRs, resulting in a lower saturation and density of Mg atoms per unit area.

The reduction in CL intensity from the \(m\)-plane facets of the NRs and tips in highly doped samples indicates an increase in non-radiative defects at or near the surface [40] or \(V_N\) acting as non-radiative recombination centers. Nitrogen vacancies have previously been proposed to form preferentially at the edges of nanowires and cluster together [48]. They have been identified in positron lifetime spectroscopy as causing compensation in p-GaN, but this effect can be mitigated through annealing, which effectively reduces the number of \(V_N\) and Mg–\(V_N\) [49]. A DAP type transition at \(~2.95\) eV [9] is expected to be dominant for Mg atom concentrations up to \(2 \times 10^{19}\) cm\(^{-3}\). However a transition to resistive and compensated p-GaN is known to occur abruptly for Mg atom concentrations above \(3 \times 10^{19}\) cm\(^{-3}\) [12]. The lack of BL indicates no significant self-compensation occurred in these samples or Mg atom concentrations at these levels.

The growth of p-GaN layers on \(c\)-plane GaN at high Mg precursor flows could lead to the formation of pyramid shaped defects and pyramidal inversion domains that give rise to emission peaks at 3.31–3.36 eV. However, in this work there was no evidence of inversion domains; the luminescence in that energy range was reduced by annealing, indicating a vacancy complex as the origin of the high-energy peaks.

Magnesium incorporation in GaN is expected to strain compressively the lattice due to the Mg atom radius being larger than the Ga atoms radius [22]. A small shift in the \(E_3^\text{DAP}\) peak, corresponding to tensile strain with higher doping was observed, both in individual NRs and in arrays of standing NRs. High resolution Raman maps revealed a gradual shift to tensile strain with the increase in Mg atom concentration. The largest variation of \(E_3^\text{DAP}\) was seen on the \(m\)-plane sidewalls in the \(highly\) doped sample. For the \(medium\) doped sample the range of \(E_3^\text{DAP}\) values was smaller, indicating the p-shell was more uniform. The distribution of compensating nitrogen vacancy complexes, \(V_N\) or Mg–\(V_N\), is considered the likely cause of the variation in strain. However, their location could only be approximate from the Raman maps.

A uniform bright band corresponding to the minority carrier collection current was observed under EBIC measurements. The as-grown samples, even after annealing, showed only local current spreading between the NR interface and the EBIC probes, characteristic of thin p-GaN layers with higher resistance. Because the design of LED devices will highly likely include large arrays of connected NRs, an ITO transparent conducting layer was used to improve current spreading and as a next step in the design of core–shell LEDs. As the EBIC signal follows the \(p-n\) junction position and width, it proves active hole carriers and a uniform junction was achieved.

5. Conclusions

Complementary measurements of room temperature \(\mu\)PL, CL, Raman spectroscopy and EBIC were used to identify Mg incorporation, p-shell growth parameters, map doping uniformity and estimate carrier concentrations for core–shell NRs. Correlation with planar Hall-effect literature values and luminescence signatures were used to make a first estimate of p-doping levels on core–shell NRs. This estimate for the number of active hole carriers was in the range of \(5 \times 10^{16}-2 \times 10^{17}\) cm\(^{-3}\). The assessment of the \(p-n\) junction width by EBIC correlates well with this initial estimate. The effects of different growth parameters, dopant concentrations and activation by thermal annealing were identified for the NRs.

DAP transitions at 3.27, 3.24 and 3.16 eV indicate the presence of Mg atoms, although likely bonded to compensating hydrogen atoms or hydrogen complexes. The DAP emission becomes less uniform at high \(Cp_2\text{Mg}\) flow, likely because of the formation of local non-radiative recombination centers, as evidenced by dark regions on the highly doped samples.
under CL. Effective annealing contributes to the formation of mobile hole carriers, as demonstrated by the reduction in intensity of the DAP peaks and the formation of a continuous p-n junction.

EBIC measurements showed the p-n junction interface was uniform in width and current intensity, indicating the regrowth method can achieve uniform and smooth p-GaN shells. A p-GaN shell with thickness around ~150–200 nm was required to provide an effective p-n junction at the doping level achieved. The 3.14 eV DAP2 peak was visible at the p-n junction interface, and could be related either to the concentration achieved, or to the active Mg-hole optical signature. Correlation of the non-contact methods and measurements in EBIC provided a practical estimate on doping concentration achieved where electrical measurement methods could not be applied.

These results show how a combination of non-contact optical characterization methods, as well as EBIC, can be used to analyze the uniformity of p-doped layers in III-nitride nanostructures and provide values for the level of doping. Thus, the techniques are essential for the development of new nanostructured electroluminescent emitters such as LEDs or LDs.

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