The effect of Mg doping on GaN nanowires

E. Cimpoiasu\textsuperscript{1,4}, E. Stern\textsuperscript{2}, R. Klie\textsuperscript{3}, R. A. Munden\textsuperscript{1}, G. Cheng\textsuperscript{1}, and M. A. Reed\textsuperscript{1}

\textsuperscript{1}Departments of Electrical Engineering and Applied Physics, Yale University, New Haven, CT, 06520
\textsuperscript{2}Department of Biomedical Engineering, Yale University, New Haven, CT, 06520
\textsuperscript{3}Brookhaven National Laboratory, Upton, NY, 11760

We present a comparison between the structural, chemical, and electrical properties of Mg-doped GaN nanowires grown by hot-wall chemical vapor deposition using two different Mg sources, namely, metalorganic bis(methylcyclopentadienyl) magnesium and magnesium nitride powder. We find that Mg from the solid nitride source is more effectively incorporated into the nanowires while better maintaining the nanowire integrity. After Mg activation, the nanowires are partially or fully compensated. In comparison, vapor-phase doping results in an obvious degradation of the nanowire morphology in spite of lower Mg incorporation levels.

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\footnote{The author to whom correspondence should be addressed; email: elena.cimpoiasu@yale.edu}
1. Introduction

Gallium nitride is a direct bandgap semiconductor of interest for ultraviolet and blue optoelectronics devices. This class of devices, which includes light-emitting diodes, requires very high quality \(pn\) junctions, and, therefore, precise doping control. To date, highly controlled \(p\)-doping of GaN has been achieved predominantly in epitaxial thin layer structures. Recently, \(p\)-type doping and \(pn\) junctions were demonstrated in quasi one-dimensional GaN structures, such as nanowires and nanorods [1-3]. Magnesium was the dopant of choice in these structures, and was delivered either from a solid source, such as magnesium nitride \(\text{Mg}_3\text{N}_2\) [2], or from a metalorganic source, such as bis(cyclopentadienyl)magnesium \((\text{Cp})_2\text{Mg}\) [3]. All reports on the electrical characteristics of as-grown GaN nanowires have shown that they grow unintentionally \(n\)-type, with large carrier concentrations of \(10^{18}\) to \(10^{19}\) \(\text{cm}^{-3}\) [4-6]. Thus, fairly large quantities of magnesium must be incorporated into the nanowires to overcome the background electron concentration due to residual donors. This can be difficult to achieve reproducibly, because less than 1\% of incorporated magnesium produces acceptor centers at room temperature due to its large activation energy of \(~200\text{meV}\) [7]. Consequently, for hole densities of \(10^{18}\) \(\text{cm}^{-3}\) at room temperature, one has to achieve high Mg concentrations of \(~10^{20}\) \(\text{cm}^{-3}\) (which are near the solubility limit for Mg [8]).

This work presents a comparison on the effect of heavy Mg-doping on the morphology, structure, chemical profile and electrical properties of GaN nanowires grown with a hot-wall chemical vapor deposition system. We have used two types of Mg sources: \(\text{Mg}_3\text{N}_2\) powder and bis(methylcyclopentadienyl)magnesium \([(\text{MeCp})_2\text{Mg}\)]. The later is less common for \(p\)-type doping of III-V alloys compared to the better known \((\text{Cp})_2\text{Mg}\), but it is structurally similar and has a higher vapor pressure. We find that both doping methods produce crystalline defects that affect the nanowire morphology, but in different ways. Particularly, we find that Mg delivered from the solid source is incorporated more efficiently and that the nanowire integrity (diameter and growth direction) is preserved. In contrast, doping using \((\text{MeCp})_2\text{Mg}\) results in an obvious degradation of the shape and diameter of the nanowires, even though less Mg is incorporated.
2. Experimental

GaN nanowires were prepared using metal-catalyzed chemical vapor deposition via vapor-solid-liquid growth mechanism in a horizontal tube-furnace at temperatures of 900°C or 950°C. Metallic gallium (99.9999%, Alpha Aesar) was placed in proximity, but upstream of the substrate (Ni-coated polycrystalline alumina), over which ammonia gas was flown. Magnesium doping was carried out using the two mentioned types of sources: metalloorganic (MeCp)$_2$Mg or magnesium nitride powder. Syntheses with (MeCp)$_2$Mg were oxide-assisted (Ga$_2$O$_3$ powder was added to increase the gallium vapor pressure) and performed at a base pressure of 300 torr. Nitrogen was used as a carrier gas for the (MeCp)$_2$Mg to set the flow rate to 59-186 nmol/min. Syntheses with magnesium nitride powder were performed in the presence of a 100 sccm ammonia flux and Ga$_2$O$_3$ powder at 900°C, or a 30 sccm ammonia flux and a 60 sccm argon flux at 950°C. Details of the growth parameters are included in Table 1.

The morphology and chemical composition of the nanowires were characterized using a field-effect scanning electron microscope and a high-resolution transmission electron microscope (JEOL 3000FTEM/STEM) with a Schottky field-emission electron-gun operated at 300 kV [9]. The electron energy-loss spectra [10] were acquired by scanning a focused probe of 0.2 nm diameter across the nanowire while collecting the inelastically forward scattered electrons in the post-column EELS spectrometer.

In order to extract the electronic properties (the type of electrical conduction, the carrier concentration and the drift mobility), individual nanowire field-effect-transistors were fabricated via optical lithography on a degenerate silicon wafer with 200 nm of thermal SiO$_2$ as the gate dielectric. The advantage of using optical lithography as opposed to electron beam lithography is that it allows parallel processing of a large number of nanowires and, in turn, constitutes a blind test of their electronic properties. In this way a large number of nanowires were electrically investigated. A detailed description of the device fabrication process can be found in Ref. 11. The carrier mobility $\mu$ and the carrier
concentration \( n \) of each nanowire device were estimated from gated current-voltage measurements using the transconductance:

\[
\frac{\partial I_{SD}}{\partial V_{GD}} = \mu \frac{C}{L} V_{SD},
\]

where \( C = \frac{2\pi \varepsilon \varepsilon_0 L}{\ln(4h/d)} \) (\( L \) is the length of the nanowire, \( d \) is the diameter of the nanowire, \( h = 200 \) nm is the oxide thickness), and the conductivity \( \sigma \) of the nanowire:

\[
n = \frac{\sigma}{e\mu}.
\]

3. Results

Our previous work [11] on metal-catalyzed unintentionally-doped GaN nanowires found that the nanowires are high aspect-ratio structures, with diameters between 10 and 150 nm and lengths approaching tens of microns for growth times of 25 minutes. The microstructure analysis indicated that these nanowires are straight (with constant diameter), crystalline (with a wurtzite structure) and grow perpendicular to the \( c \)-axis, along the \(<02\bar{1}1>\) direction.

The incorporation of Mg is expected to affect the electrical properties and the microstructure of the nanowires, especially at high doping levels (which are necessary to overcome the innate \( n \)-type background of the nanowires). We first sought to determine the affect of metaloorganic Mg doping on GaN nanowires. Figure 1 is a field emission scanning electron micrograph (FE-SEM) of representative nanowires grown using \((\text{MeCp})_2\text{Mg}\) at two very different increasing flow rates: 59 nmol/min [Figure 1(a); Sample A] and 186 nmol/min [Figure 1(b); Sample C]. A clear degradation of the nanowire morphology is observed at high dopant flow rate [see Figure 1(b)], namely, the nanowires acquire a “tape-like” morphology, with multiple kinks and variable diameter along the length of the nanowire. This degradation is better demonstrated in Figure 1(c), which is a high resolution TEM micrograph of a
nanowire from Sample B. The Mg-doped GaN nanowire exhibits variable diameter indicative of high numbers of dopant-induced defects.

The effect of Mg incorporation into nanowires from the magnesium nitride powder source is different. The nanowire morphology changes from straight in the undoped or lightly-doped case [Figure 2(a); Sample D] to highly bent at higher doping levels [Figure 2(b); Sample E]. Interestingly, though the nanowires from Sample E are bent, their diameters are uniform and the growth direction is preserved. This is better illustrated in the TEM of a representative nanowire in Figure 2(c). The streaks along the axis of the nanowire are observed in the majority of the bent nanowires and have a similar appearance with defects reported in bulk Mg-doped GaN [12] and MBE-grown Mg-doped GaN thin films [13], indicating that they are most likely stalking faults along the c-axis direction of the wurtzite structure.

To study the incorporation of Mg into our nanostructures, we performed electron energy-loss spectroscopy (EELS). The integrated spectrum intensities multiplied by the elemental cross-section across two nanowires, one from Sample B [(MeCp)2Mg] and one from Sample E (Mg3N2), are shown in Figures 3(a) and 3(b), respectively. The concentrations of four species—nitrogen, oxygen, silicon and magnesium—are monitored in each plot. As illustrated in the FE-SEM inset in Figure 3(a), the profiles in both panels begin (0 nm) at the nanowire edge and proceed towards the core. The onset of the nanowire core corresponds to the onset of the nitrogen signal, which begins at ~20 nm. Silicon and oxygen are present in both Sample B and Sample E nanowires, but with noticeable differences in their EELS profiles, indicative of possible fundamental structural differences. Namely, the EELS spectra of Sample B [Figure 3(a)] show that the silicon level is constant throughout the wire, while the oxygen level is constant over the outer 20 nm (position which corresponds to the onset of the nitride nanowire core), but afterwards decreases gradually towards the core of the wire. This decrease appears to correlate with the increasing nitrogen signal [see Figure 3(a)]. One possible interpretation of these EELS profiles would be a Si-doped GaN core surrounded by an amorphous GaOx shell. Although Mg is present in the nanowire, it is barely detectable, indicating a concentration of less than ca. 1 atomic %, which is the instrument sensitivity. This is, however, consistent with expected Mg doping levels of approximately 10^{20} \text{atoms/cm}^3 (\approx 0.23
atomic\%) [2]. As opposed to the sample B nanowire, the EELS spectra of the Sample E nanowire [Figure 3(b)] show that Si and O profiles are correlated, namely, their levels are high over the outer ~25 nm, but decrease sharply towards the nanowire core to below than (for Si) or close to (for oxygen) the instrument sensitivity. These EELS spectra are consistent with a GaN nanowire core, surrounded by a SiO\textsubscript{2} shell. The magnesium signal rises in parallel with the N signal (therefore clearly doping the GaN nanowire core) to higher concentration levels this time, estimated at approx. 3.6 atomic \%. This value represents a concentration of magnesium of $\approx 10^{21}$ atoms/cm\textsuperscript{3} which corresponds to the heavily doped regime [14]. The strong presence of silicon [15] and oxygen is undesirable, as they can be responsible for the $n$-type behavior, together with the possible nitrogen vacancy donors formed during growth. On the other hand, codoping of Mg-doped GaN with shallow donors like O and Si has been proposed as a way to increase the solubility limit of either impurity [16] and has been demonstrated to improve the p-type conductivity of GaN this films (Ref. [17] and references therein).

In order to establish if Mg-doping produces acceptor centers, we have fabricated the nanowires into field-effect transistors (FETs). A sample with nominally identical growth conditions to Sample B and another with nominally identical growth conditions to Sample E were annealed after growth at 750°C for ~15 min (necessary for the activation of the Mg acceptor centers) and the nanowires were then fabricated into electrical devices. Results on nanowires from Sample B were electrically similar to unintentionally-doped controls ($n$-type, data not shown). This finding is consistent with the EELS data indicating a concentration of Mg that is most likely insufficient to effectively compensate the relatively large concentration of donors, coming from silicon and oxygen. Devices from the annealed Sample E nanowires exhibited $n$-type conduction as well, but the carrier concentrations achieved are lower compared to the as-grown, undoped nanowires. This is illustrated in Figure 5, which plots drift mobilities vs. carrier concentrations for two unintentionally-doped ($n$-type, as-grown) GaN samples (one of which was achieved after optimizing the growth parameters [18]) and a number of epitaxial thin-film GaN samples [19]. The FE-SEM inset shows a representative device from the Mg-doped GaN nanowire sample; the Mg-induced nanowire bending is preserved through device processing. As reported
previously, the as-grown nanowires are highly $n$-type doped, with carrier concentrations of $\sim 10^{19}$ to $10^{20}$ cm$^{-3}$, most probably due to a combination of oxygen impurities and nitrogen vacancies. The Mg-doped GaN nanowires are seen to have both lower mobilities and carrier concentrations (down by approximately one order of magnitude, to the lowest of $2 \times 10^{18}$ cm$^{-3}$). In addition, the Mg-doped devices exhibit a trend of increasing mobility with increasing carrier concentration, the opposite of that for the unintentionally-doped nanowires. It is also observed that there are greater device-to-device fluctuations for Mg-doped nanowires as for their counterparts. Taken together, these data suggest that Mg is being successfully activated as a $p$-type dopant, but not to the optimal concentration that would compensate the $n$-type behavior. The above findings are consistent with compensation doping, which reduces both the carrier concentration and mobility because of the increased number of scattering centers, and enhances device-to-device fluctuations due to the random nature of Mg incorporation and activation.

We then explored the effect of more severe annealing conditions. Two additional samples with nominally identical growth conditions to Sample E were annealed in flowing nitrogen at 750$^\circ$C for 60 min and at 800$^\circ$C for 30 min. Electrical measurements on devices from both samples were similar, and showed that these nanowires had significantly higher resistances, $10^{11}$ to $10^{12}$ $\Omega$, as compared with those of the nanowires from the first Mg-doped sample, which were between $10^6$ and $10^8$ $\Omega$. Assuming that greater activation exposure (time or temperature) produces more acceptor centers, it follows that the sample with the smallest activation exposure is partially-compensated $n$-type, while the samples with larger activation exposures are fully-compensated, therefore, highly resistive. The inability to demonstrate $p$-type behavior is most likely due to the high background $n$-type carrier concentration that must be entirely compensated.

4. Conclusion

We have studied the effect of Mg-doping during growth on the morphology, chemical profile, and transport properties of GaN nanowires grown by hot-wall chemical vapor deposition. Magnesium was successfully incorporated into nanowires grown with two Mg sources, vapor-phase (MeCp)$_2$Mg and
Mg$_3$N$_2$ powder, but each source was found to affect nanowire morphology and electrical transport differently. High flows of (MeCp)$_2$Mg produce greatly deformed nanowires, with variable diameters and multiple kinks, at Mg incorporation levels of roughly $10^{20}$ cm$^{-3}$. Magnesium nitride powder produces nanowires that are bent, but otherwise unaffected morphologically in spite of the very high Mg concentrations (3.6 at.% $\approx 10^{21}$ cm$^{-3}$). Electrical characterization of annealed samples shows that vapor-phase-doped nanowires have similar transport properties to undoped, as-grown nanowires, while solid-source-doped nanowires show clear signs of compensation due to the presence of Mg acceptor centers.

Acknowledgements

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References:


15. The presence of silicon was not intentional and potential sources of contamination might relate to the following (a) the growth is a hot-wall process and there might be chemical interaction between the gas phase dopants and quartz-reactor wall [Richard L. Molnar in “Gallium Nitride
(GaN) II, Semiconductors and Semimetals”", vol. 57, ed. J.I. Pankove and T.D. Moustakas, 1999, pg. 11] and (b) during few growth runs, oxide-covered silicon chips have been used as growth substrates or support for the gallium species.


Table 1. Growth parameters of the Mg-doped GaN nanowires

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<th>Sample</th>
<th>Mg source</th>
<th>Ga source</th>
<th>Temperature(°C)</th>
<th>Gas Flow (secm)</th>
<th>Pressure (torr)</th>
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<td>(MeCp)$_2$Mg</td>
<td>Ga&amp;Ga$_2$O$_3$</td>
<td>950</td>
<td>NH$_3$, 100</td>
<td>300</td>
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<td>B</td>
<td>(MeCp)$_2$Mg</td>
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<td>900</td>
<td>NH$_3$, 100</td>
<td>300</td>
</tr>
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<td></td>
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<td>111 nmol/min</td>
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<td>C</td>
<td>(MeCp)$_2$Mg</td>
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Figure captions:

Figure 1. FE-SEM micrographs of Mg-doped GaN nanowires grown using (MeCp)$_2$Mg at (a) 59 nmol/min, Sample A and (b) 186 nmol/min, Sample C. (c) TEM micrograph of a (MeCp)$_2$Mg-doped GaN nanowire from Sample B.

Figure 2. FE-SEM micrographs of Mg-doped GaN nanowires grown using Mg$_3$N$_2$ powder at (a) 900°C, Sample D and (b) 950°C, Sample E. (c) TEM micrograph of a Mg$_3$N$_2$-doped GaN nanowire from Sample E.

Figure 3. Profiles of four species of interest, Si, O, N, and Mg for a representative nanowire from (a) Sample B and (b) Sample E, as extracted using EELS. The solid lines represent the smoothed profiles. The inset FE-SEM shows the direction and orientation of the scan, which begins at the nanowire edge (0 nm).

Figure 4. Plot of drift mobility vs. carrier concentration. Filled squares correspond to devices from Sample E, while empty circles and crosses correspond to unintentionally-doped (as-grown) nanowires [18]. Data from epitaxially-grown thin-film GaN [19] is plotted as filled triangles. The inset shows a FE-SEM micrograph of a nanowire device.
Figure 1
Figure 2
Figure 3

(a) Mg concentration
(b) N concentration
O concentration
Si concentration
Figure 4