Characterizing Atomic Composition and Dopant Distribution in Wide Band Gap Semiconductor Nanowires Using Laser-Assisted Atom Probe Tomography

Ravi Agrawal,† Rodrigo A. Bernal,‡ Dieter Isheim,‡ and Horacio D. Espinosa*,†

†Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3111, United States
‡Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, Illinois 60208-3108, United States

Supporting Information

ABSTRACT: Characterization of atomic composition and spatially resolved dopant distribution in wide band gap semiconducting nanowires is critical for their applications in next-generation nanoelectronic and optoelectronic devices. We have applied laser-assisted atom probe tomography to measure the spatially resolved composition of wide band gap semiconducting undoped GaN nanowires and Mg-doped GaN nanowires. Stoichiometric evaporation of individual GaN nanowires was achieved, and optimal experimental conditions to characterize the concentration and spatial distribution of the dopant in the Mg:GaN nanowire samples were established. Extremely mild operating conditions, with laser pulse energy as low as 3 pJ, are required to avoid preferential loss of nitrogen and achieve stoichiometric evaporation. The role of nanowire morphology in the selection of optimal experimental conditions is discussed in the context of thermal transport within the nanowire under a heat load imposed by the pulsing laser. The results of this work are expected to help guide similar atom probe tomography studies of related wide band gap III–V semiconductor alloys, which will facilitate a better understanding of material response and will help develop structure–property relationships.

One-dimensional semiconducting nanostructures are envisioned as building blocks for emerging high-performance piezoelectric and optoelectronic devices. The exceptionally low defect density, dense columnar morphology, and high light-extraction efficiency of arrayed GaN nanowire LEDs make such technology a compelling new approach to high efficiency solid-state lighting. Use of semiconductor nanoscale morphologies (nanowires, nanobelts, etc.) is also the path being taken for further miniaturization of CMOS devices. The techniques to grow such nanostructures in a controlled manner based on vapor–liquid–solid (VLS) growth, solid–liquid–solid (SLS) growth, and molecular beam epitaxy (MBE) are quite developed. However, to exploit these nanoscale components to their full potential, appropriate characterization of their properties, including local composition and structure, is necessary. It is well-known that the electronic properties of semiconducting materials can be greatly influenced by the presence of intentional or unintentional impurities arising from the growth processes. In bulk materials and epitaxial films, techniques such as Hall measurements and capacitance—voltage (C–V) profiles are used to measure free carrier concentration n and infer the doping level (using foreknowledge of dopant ionization). Secondary ion mass spectroscopy (SIMS) is often used to directly measure atomic concentrations of dopants and impurities. Because of the small dimensions and 3D morphology often encountered in nanostructures, traditional Hall and C–V methods may be extremely difficult or impossible to apply.

A common technique to estimate n and μ (electron mobility) in semiconductor nanowires (NWs) relies on measuring the behavior of NW field effect transistor (FET) test structures and fitting the experimental results to device simulations. This approach is hampered by a number of factors including the electrical contact resistivity, the nature of the gate (e.g., back-gated, top-gated, conformally gated, use of a gate oxide layer, or use of a Schottky gated structure) and its influence on parasitic capacitance, the true cross-sectional morphology and dimensions of the NW, etc. The complex 3D nature of the device geometry generally necessitates the use of full 3D numerical Poisson and drift-diffusion simulation codes to accurately infer n and μ. Nonetheless, depending on the level of approximation and accuracy of the modeling used, variations in fitted values of μ may be rather high; values ranging from 2 to 600 cm2 V−1 s−1 have been reported. Moreover, other parasitic effects that are difficult to quantify (such as long-lived traps in gate oxides) may

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lead to hysteresis artifacts in FET behavior that further complicate simulating FET behavior. These efforts illustrate that accurate correlation between $n_i$, $\mu$, and the NW growth process (and wire growth habit) is difficult if not impossible to extract from FET behavior even with the modern simulators available. Recently, transient and steady-state photoconductivity in NWs was used as an alternative scheme to estimate NW transport properties.11

These difficulties emphasize the need of a direct quantitative assessment of doping distribution and concentration in the NW specimens without the need to infer such information from device behavior. SIMS is well suited to planar thin films and can be applied to a certain extent to the quantitative analysis of as-grown NW samples. However, the dense 3D NW growth morphology leads to uneven etching and melting of some sample regions when SIMS analysis is attempted. The conventional elemental analysis techniques like electron energy loss spectrum (EELS) and X-ray fluorescence are limited to detect concentrations of approximately $5 \times 10^{10}$ cm$^{-3}$, whereas dopant concentrations of interest in the GaN NWs of consideration herein generally range from roughly $10^{15}$ to $10^{20}$ cm$^{-3}$.12 Such resolution is achievable with laser-assisted atom probe tomography, which offers sensitivity at the level of $5 \times 10^{17}$ cm$^{-3}$ or 10 appm.13 However, the application of this approach to wide band gap compound semiconducting materials, in particular to NWs, is limited because of various challenges associated with the specimen preparation and experimental conditions required to obtain accurate stoichiometry.

In atom probe tomography (APT), atoms at the specimen surface are field evaporated as ions in a high electric field by a thermally activated process.14 The specimens are needle-shaped roughly 20–200 nm in diameter and a few micrometers in length. The experimental embodiment generally requires the sample held in a UHV chamber and cooled to temperatures as low as 20 K. In the 1980s, the use of pulsed lasers was explored to make less conductive materials like semiconductors and metal oxides accessible for what then was called pulsed-laser atom probe.15 The importance of laser pulse energy as an experimental parameter was recognized early.16 A high electric field was still applied to cause field evaporation and to provide directionality to the flight path of evaporated atoms. While pioneering work was conducted then, the stability of the lasers available in the 1980s and difficulties with controlling evaporation limited applications.17

In the late 1990s, a variation of APT called local electrode atom probe (LEAP) tomography was introduced.18,19 In this configuration, an electrode was placed within $30 \sim 40 \mu$m of the specimen. This scheme reduced the voltages necessary to achieve field evaporation. In the past decade, technologically improved lasers were added to commercially available APT systems, leading to a renaissance of APT studies specifically of electronic materials.17 In addition, advances in 2D area detectors, time-of-flight mass spectroscopy, and analytical software now permit a full 3D atom-by-atom “reconstruction” representation of the field-evaporated sample. The reconstructed portion of the sample corresponds to the core (or central region) of the specimen and the reconstructed diameter can vary between 20 and 250 nm depending on the instrument field of view and other experimental conditions. In the laser-assisted LEAP configuration, the pulsed laser provides temporal gating of the field-emitted ions while the electric biasing field is held constant. Throughout this Article, it is understood that the expression “laser-assisted atom probe tomography” is synonymous with LEAP as previously defined.

In the context of investigating semiconducting NWs using LEAP, a few prior studies exist on Si,20,21 Ge,22 and InAs23 NWs, where the NWs were directly grown on prefabricated silicon microposts designed for the LEAP setup. This poses a limitation that only the NWs that can be grown on microposts can be studied. In this work, we used an alternative technique utilizing nanomanipulation that should in principle allow for LEAP analysis of any kind of NW. In addition to sample preparation, a major challenge to study a compound semiconductor like GaN (as opposed to Si or Ge) is the ability to achieve the correct stoichiometric composition of Ga and N in single crystal defect-free specimens. In terms of compound semiconductor NWs, only InAs NWs (with band gap $\sim 0.4$ eV) have been investigated earlier, and the samples used in that study were relatively conductive (at room temperature) as compared to GaN NWs of the present study.24,25 The higher band gap in GaN ($\sim 3.4$ eV) possibly posed additional challenges as presented in this work.

Individual NWs were manipulated and mounted at the end of a tungsten (W) probe (see the Supporting Information and Figure 1). The W probe with the mounted NWs was then aligned in front of the local electrode, as shown in Figure 2a. Three types of NWs were studied: A, B, and C (see the Supporting Information for details of growth process). A-type NWs were undoped and had a uniform diameter in the 100–130 nm range as shown in Figure 2b. B- and C-type NWs were Mg-doped and grew with a tapered morphology (Figure 2c). The taper angle was $\sim 0.5^\circ$, and the diameter at the tip ranged from 30 to 60 nm. In all of the cases, the cross-section was hexagonal and the length of the mounted NWs ranged from 5 to 9 $\mu$m. The various specimens studied and their dimensions are summarized in Table 1.

GaN can only exist within a narrow homogeneity range near 50% Ga and 50% N composition. It is unlikely that the composition deviates by more than 0.1 atomic percent of nitrogen from exact stoichiometry. We found that the relative composition recorded by LEAP was greatly influenced by the experimental conditions, primarily the laser energy being used to assist the evaporation of atoms. Under nonoptimal conditions, N was disproportionally lost, and we observed the measured yield of N atoms to be as low as 20% in some experiments. We analyzed the effect of different experimental parameters, laser pulse frequency, laser energy, and specimen base temperature, on the compositional results obtained for various NWs specimens. The experimental conditions and results are discussed next.

Figure 2e summarizes the apparent nitrogen composition obtained by LEAP tomography for all specimens at different experimental conditions. Changing the laser pulse frequency, while keeping other experimental conditions the same, did not
significantly affect the measured composition. For example, the LEAP derived N composition varied by less than 1% over a range of pulse frequency from 250 to 500 kHz (case 7 and case 8 in Figure 2e). However, we observed that specimen failure at the platinum weld that attached the NW to the W probe (Figure 2b, see the Supporting Information) occurred more often at the higher laser pulse frequencies and that the signal-to-noise ratio in the mass spectrum decreased with increasing laser pulse frequency. Therefore, lower laser pulse frequencies in the 200–250 kHz range were used in all other measurements. The most important parameter that influenced the LEAP derived compositional measurements was laser pulse energy. This is evident from the results illustrated in Figure 2e. It was observed that the apparent N content increased and approached a stoichiometric value of 50% as the laser pulse energy was decreased to values of 3 pJ (for undoped samples) and 20 pJ (for doped samples). Below these critical values, the N content was found to be stoichiometric; however, the signal-to-noise ratio got worse (due to DC evaporation), which is detrimental for the determination of dopant concentrations. It was also observed that the charge-state-ratio (CSR) of Ga+/Ga^{2+} ions increased with pulse energy and therefore was inversely correlated with the apparent N composition (Figure 2f). Figure 2d shows the mass spectra for A-type sample (for case 1 and case 2), normalized with respect to Ga^{+} peak. This figure illustrates the observed trend that the height of N peaks increases with Ga^{2+} peaks. Peaks corresponding to Ga^{3+} ions also emerged at lower laser energy (case 1). The charge state of the field evaporated ions is a sensitive measure for the strength of the local electric field at the specimen tip, with higher electric fields resulting in a higher probability for a higher charge state.26,27 Because field evaporation is also thermally activated, at the higher temperatures produced with higher laser pulse energy, a lower electric field is needed to sustain a given evaporation rate. Because the instrument automatically adjusts the electric field to maintain a targeted evaporation rate, the field used in higher energy runs is lower, and fewer doubly and triply charged ions are generated.27 It is also worth mentioning that primary peak contributing to the nitrogen concentration is at N_{2}^{+} and not N^{+} or N_{2}^{2+}. Furthermore, N^{+} and N_{2}^{2+} peaks were

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**Table 1. Experimental Conditions Used for Different Specimens Studied and Plotted in Figure 2e, f**

<table>
<thead>
<tr>
<th>case sample no.</th>
<th>sample type</th>
<th>NW tip diameter (nm)</th>
<th>NW length (μm)</th>
<th>base temperature (K)</th>
<th>laser pulse frequency (kHz)</th>
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<td>6.3</td>
<td>20</td>
<td>200</td>
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<td>A</td>
<td>96</td>
<td>6.4</td>
<td>25</td>
<td>200</td>
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<td>6.4</td>
<td>20</td>
<td>200</td>
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Figure 2. Experimental setup and results: (a) An optical image showing the focused laser illuminating the tip of a NW attached to a W probe with the latter aligned in front of the local electrode. (b) SEM micrograph of an A-type (untapered and undoped) sample mounted on the W probe. (c) SEM micrograph of a C-type (tapered and Mg-doped) sample. (d) Mass spectra for A-type sample at two different laser energies, case 1 and case 2 in (e). The two spectra are normalized with respect to the ^{69}\text{Ga}^{+} peak. (e) Apparent nitrogen concentration measured as a function of laser pulse energy for various specimens. (Middle) Legend relating the data set with specimen and corresponding experimental conditions are described in Table 1. (f) Nitrogen concentration versus Ga charge-state ratio (Ga^{+}/Ga^{2+}) for different specimens.
deconvoluted by observing the \((^{14}N^{15}N)^{+2}\) peak at 14.5 amu, which is not present and implies that \(N^+\) dominates.

The effect of specimen base temperature \((T_b)\) correlated with laser pulse energy; that is, when \(T_b\) was higher, lower laser pulse energy was required to obtain a given composition. This trend is evident, for instance, from the results corresponding to case 6 \((T_b = 80 \, K)\) and case 7 \((T_b = 40 \, K)\) in Figure 2e. Together with the dependence of the charge-state-ratio on pulse energy discussed above, this confirms that higher laser energies correspond to higher sample temperatures. Because of equipment limitations, the minimum calibrated laser pulse energy was 2 pJ for the LEAP tomographs used here. Therefore, lower sample temperatures were preferred so that relatively higher laser pulse energies could be utilized. This was particularly important for A-type samples, as an order of magnitude smaller energy was required for optimal composition measurement. The difference in laser pulse energies observed for A-type and B- and C-type samples to obtain \(50\% \pm 1\%\) at. \% of \(N\) may be attributed to coupled effects of (i) difference in their geometries and (ii) increase in thermal/electrical conductivity with doping. To explore these effects, we investigated the thermal transport in NWs of different geometries, which is discussed later.

To explore the effects of laser pulse energy on the evaporation of atoms from the NW samples, two cases (1 and 2) for the A-type samples were analyzed (mass spectra for which are shown in Figure 2d). Using advanced data analysis software packages developed specifically for LEAP, the accumulated time-of-flight mass spectra of the evaporated NWs were “reconstructed” to yield 2D profiles of composition of \(N\) and \(Ga\). The density of \(Ga\) and \(N\) atoms was calculated using data that were sampled along the entire length of the evaporated NW. Figure 3 shows such 2D composition and density profiles along the cross-section of the NW. Notice that the density profiles revealed the crystallographic pole and 6-fold symmetry in agreement with the stereographic projection along the (0001) direction of the wurtzite hexagonal crystal structure of \(GaN\) (Figure 3c). As shown in Figure 3a, during optimal experimental conditions (case 1, 50% \(N\)), the \(N\) is distributed uniformly across the cross-section. However, at higher laser energy (case 2, 34% \(N\), Figure 3b), the distribution is nonuniform and the \(N\%) reduces away from the pole. This is also confirmed from the density profiles of \(Ga\) and \(N\) atoms. When the \(Ga\) and \(N\) constituent ratios are \(\sim 50\%\) within experimental error, the density of both types of atoms varies in the same manner over the cross-section (Figure 3c,e). A variation of atomic density over the cross-section of an atom probe tomography reconstruction is not unusual and is related to a variation of the radius of curvature for different crystallographic directions.26 This effect, however, should affect all atomic species in the same way, which is not the case at higher laser pulse energy (see Figure 3d and f). At the higher energy, the density of \(Ga\) atoms follow the same pattern (compare Figure 3e and f), but the density of \(N\) is reduced in the regions away from the pole, suggesting that \(N\) is lost at higher temperature due to preferential field-evaporation in between the laser pulses.

The preferential loss of \(N\) atoms and the observation of nonuniform distribution of at. \% of \(N\) (Figure 3a vs b) over the cross-section at higher laser pulse energies suggests that the tip of the NWs was not being heated uniformly. To validate this hypothesis and to further understand the experimentally observed trends for different kinds of NWs, thermal transport was modeled using the finite element method. The objective of this modeling was 2-fold: (i) to examine the thermal transport as a function of laser pulse energy; and (ii) to decouple the effect of geometry from possible improvement in electrical/thermal conductivity due to the incorporation of dopants. Because bulk GaN is essentially transparent to 532 nm laser wavelength, nanowire heating was assumed to be a result of surface absorption. Various mechanisms of surface absorption have been reported in the literature including band bending at surfaces and optical transitions involving occupied surface states to the conduction band.11,28,29 The heat absorption mechanism is beyond the scope of this Article. However, knowing it to be a surface phenomenon, the heat induced by the laser was modeled to be on the surface with negligible skin depth. Three NW geometries were modeled: (i) an untapered NW with 120 nm diameter, representing the A-type wires (Figure 4a); (ii) a tapered wire with taper angle of \(0.5^\circ\) and 40 nm tip diameter, representing the B- and C-type wire; and (iii) a tapered NW with 120 nm tip diameter and same taper angle. A Gaussian heat profile was modeled, similar to that of the laser, exponentially decaying with time:

\[
S = \frac{S_0}{2\pi \sigma^2} \exp \left( -\frac{t - t_0}{t_d} \right) \left[ \exp \left\{ -\frac{1}{2\sigma^2} (x^2 + z^2) \right\} \right]
\]

where a decay time \((t_d)\) of 10 ps30 and \(\sigma\) (representative of laser spot size) of 1.0 \(\mu\)m were used based on the observation of evaporation profiles during the experiment. \(S_0\) is representative of laser energy intensity, \(t_0\) is the time at which laser is exposed on the specimen in the model, and \(x\) and \(z\) are the spatial coordinates.
with origin at the center of the laser spot. In the region outside the spatial domain of the NW, $S = 0$. The heat source was centered at the tip of the NW, that is, at $x = 0$ and $z = 0$ in Figure 4b,c. $S_0$ was varied so as to vary the energy supplied to the NW. The total thermal energy associated with this Gaussian distribution (obtained by integrating the expression for $S$ over the entire space) is given by $E = t_0 S_0$ and was varied between $10^{-21}$ and $10^{-17}$ nJ. The total thermal energy qualitatively represents the laser pulse energy, if the absorption coefficient is accounted for. See the Supporting Information for further details.

Figure 4d shows the temperature evolution of the laser illuminated side of the NW (solid line) and the shadowed back side of the NW (dashed line) as a function of time at $z = 0$. These temperature profiles reveal three things under the assumption that the optical absorption coefficient is the same irrespective of the sample type: (i) A temperature gradient is present across the cross-section of the wire (i.e., between the illuminated side and the shadowed side), which decays with time; (ii) this transverse temperature gradient diminishes as the laser energy is lowered; and (iii) for the same laser pulse energy, less time is required for the thinner NWs to attain a negligible transverse temperature gradient. In addition, after the decay of the transverse temperature gradient, temperature profiles were extrapolated to estimate the time required for the NW tip to cool to the base temperature. On the basis of exponential extrapolation, the cooling times were found to be within 150 ns for all of the NW cases modeled, which is much smaller than 5 μs duration between two subsequent laser pulses at 200 kHz but orders of magnitude longer than the laser pulse. The effect of taper on temperature profiles was found to be insignificant. The nonuniform heating of the NW tip can be attributed to unusually low thermal conductivity of GaN NWs.31 Because the detector is synchronized with the pulsing of the laser, we hypothesize that the temperature gradient that exists for times much longer than the pulse decay time can cause thermal evaporation of relatively lighter nitrogen atoms leading to their loss in the form of gaseous nitrogen ($N_2$). These findings are consistent with the experimental observation of nonuniform evaporation of $N$ across the cross-section when the energies are higher than optimal. To add a quantitative assessment of thermal loss of $N$ in between pulses, we defined a nondimensional term $\gamma$:

$$\gamma = \frac{\int (T_{\text{laser}} - T_{\text{back}}) \, dt}{t_0 (T_m - T_{\text{base}})}$$

where $T_{\text{laser}}$ and $T_{\text{back}}$ are the time-varying temperatures of the laser side and back side of the NWs, $T_{\text{base}}$ is the initial temperature (set to 40 K in all of these calculations), and $T_m$ is the decomposition temperature of GaN in a vacuum (800 °C). Figure 4e shows the variation of $\gamma$ with energy. It is noteworthy that for the same amount of thermal loss to happen (shown by the dotted line in Figure 4e), the 40 nm NW can tolerate $\sim 8$ times more laser energy, which is qualitatively consistent with the experimental results shown in Figure 2e. This suggests that
Figure 5. Dopant distribution: (a) mass spectra for two C-type samples studied (tilted vs aligned axially); (b) zoom-in showing that the Mg peaks were observed only in the tilted specimen; and (c,d) atomic reconstructions showing the axial and radial distribution of Mg atoms as seen by the detector.

geometry (particularly the diameter at the NW tip) plays a significant role in determining the optimal experimental conditions to minimize the thermal loss of N and achieve stoichiometric evaporation. Even though the crystal anisotropy and the actual tip shape during the experiment are not accounted for in the continuum-based modeling pursued here, the qualitative insight gained regarding the thermal behavior is consistent with the experimental findings. Moreover, dopant concentrations in B- and C-type samples (as shown in the next section) were found to be less than 1000 ppm (i.e., <1 Mg atom in 20 nm³ volume), which also suggests that the effect of dopants on thermal transport in the NWs may not be significant.

For the B-type samples, the peaks corresponding to Mg atoms were not observed in the spectra, suggesting that their concentration might be below the detection limit. The tapered morphology, which is an outcome of the growth conditions in the presence of dopant precursors, still asserts that there should be Mg atoms.

For C-type samples, we observed the peaks corresponding to the three isotopes of Mg in one case (case 10) and not in the other case (case 9). Mass spectra for these two cases are overlaid and shown in Figure 5a,b. Figure 5c,d shows the 3d reconstruction of the specimen in which Mg atoms were observed. The Mg concentration was measured to be ~663 ppm or 6 × 10⁻⁹ Mg atoms/cm³, after correcting for the preferential loss of N observed in this particular case. It is noteworthy that the Mg atoms are not distributed uniformly across the cross-section of the detector (Figure 5d), which suggests that the dopant concentration might be higher near the surface of the wire. This region may correspond to the material grown during the final cooler stage of growth. This argument is also validated by the fact that a 6-folded symmetry in this case was not observed, meaning that the axis of the wire was not aligned perpendicular to the local electrode. For case 9, where the Mg peaks were not observed, the 6-folded symmetry was observed. This asserted that, for these samples, alignment with respect to the local electrode might affect observation of the dopants, which seem to be dominated on surfaces. To confirm this hypothesis, one experiment was conducted with sample well aligned perpendicular to the local electrode. Initially during this run, no Mg peaks were detected; however, on moving the sample to left/right or top/bottom with respect to the center of local electrode, Mg peaks were observed. This test confirmed that Mg was primarily present on the surface of the nanowires. With the current state-of-the-art methodology of mounting and aligning NWs for LEAP experiments, it is not possible to precisely control alignment. Therefore, for investigating NWs, where dopant profiles can vary with diameter, the field of view of the detector should be larger such that the evaporation from the entire cross-section can be detected when the NWs are well-aligned.

The experimental findings reported here suggest that optimized operating conditions are required to achieve proper stoichiometric field-evaporation of GaN NWs in APT. The optimal conditions depend on the specimen geometry and thermal/electrical conductivity, and the actual optical absorption of the pulsed laser focused on the NW tip. The thermal transport modeling suggests that NW diameter plays a role. Because of extremely low thermal conductivities, smaller diameters result in more uniform laser heating across the cross-section of NW. The knowledge of absorption response at very low temperatures can further improve the model presented here for a more quantitative comparison with the experiments. Nonetheless, even within the constraint of low optical absorption, the experiments reveal that the pulsed laser operating at 532 nm and laser pulse energies <~3 pJ are required for obtaining stoichiometric measurements. Also, for the NWs with significant taper, the tip diameter will increase with evaporation during the experiment. Therefore, energies should be kept low enough to be optimal for all of the possible diameters. Such low energies lie close to the lower limit of the energy range generally available with the LEAP instrument available to us. In addition, as the absorption response of the semiconducting materials can be greatly influenced by the laser wavelength, the possibility of having multiple lasers in the same setup may be a preferred approach. In Mg-doped (C-type) samples, we measured Mg concentrations as low as ~600 ppm (~6 × 10⁻⁹ cm⁻³). However, the observation of dopants seems to depend on the tilt of the specimen with respect to the detector as the Mg seems to be dominantly present closer to the surfaces of the NWs. In summary, the challenges associated with analyzing GaN NWs using LEAP are highlighted. Experimental protocol and optimal conditions have been identified to achieve proper stoichiometry in GaN NWs, which is a prerequisite for accurate characterization of dopant concentrations. The experimental findings and the analysis presented here may assist in developing LEAP procedures for other wide band gap semiconductors or highly insulating materials.

ASSOCIATED CONTENT

Supporting Information. NW growth process, LEAP sample preparation and experimental details, and thermal
transport modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**

*Phone: (847) 467-5989. Fax: (847) 491-3915. E-mail: espinosa@northwestern.edu.*

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**REFERENCES**


