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Impact of Defects on the Electrical Transport, Optical Properties and Failure Mechanisms of GaN Nanowires

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Impact of Defects on the Electrical Transport, Optical Properties and Failure Mechanisms of GaN Nanowires

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Abstract

We present the results of a three year LDRD project that focused on understanding the impact of defects on the electrical, optical and thermal properties of GaN-based nanowires (NWs). We describe the development and application of a host of

experimental techniques to quantify and understand the physics of defects and thermal transport in GaN NWs. We also present the development of analytical models and computational studies of thermal conductivity in GaN NWs. Finally, we present an atomistic model for GaN NW electrical breakdown supported with experimental evidence.

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1. INTRODUCTION

GaN-based nanowires are attractive for applications requiring compact, high-current density devices such as ultraviolet laser arrays. Understanding GaN nanowire failure at high-current density is crucial to developing nanowire (NW) devices. Nanowire device failure is likely more complex than thin film due to the prominence of surface effects and enhanced interaction among point defects. Understanding the impact of surfaces and point defects on nanowire thermal and electrical transport is the first step toward rational control and mitigation of device failure mechanisms. However, investigating defects in GaN NWs is extremely challenging because conventional defect spectroscopy techniques are unsuitable for wide-bandgap nanostructures. To understand NW breakdown, the influence of pre-existing and emergent defects during high current stress on NW properties will be investigated. Acute sensitivity of NW thermal conductivity to point-defect density is expected due to the lack of threading dislocation (TD) gettering sites, and enhanced phonon-surface scattering further inhibits thermal transport. Excess defect creation during Joule heating could further degrade thermal conductivity, producing a vicious cycle culminating in catastrophic breakdown. To investigate these issues, a unique combination of electron microscopy, scanning luminescence and photoconductivity implemented at the nanoscale will be used in concert with sophisticated molecular-dynamics calculations of surface and defect-mediated NW thermal transport. This proposal seeks to elucidate long standing material science questions for GaN while addressing issues critical to realizing reliable GaN NW devices.

2. GROWTH OF GAN NANOWIRES AND DEVICE PATTERNING

Unintentionally doped (UID) NWs were grown via metal organic chemical vapor deposition (MOCVD) on *r*-plane sapphire using a thin (2 nm) Ni film deposited by e-beam evaporation as the catalyst for vapor-liquid-solid- (VLS-) based growth.¹ Growth was carried out for 5 minutes at a substrate temperature of 900 °C and a pressure of 450 Torr. III-V growth precursor flows were 95 sccm H₂ through a trimethylgallium bubbler at a temperature of 20 °C and 16,000 sccm

ammonia. Growth under these conditions yielded highly aligned NWs grown along the $[11\bar{2}0]$ direction with single crystallinity, wurtzite structure and triangular cross-sections. Homoepitaxial GaN sidewall growth concurrent with VLS-type axial growth likely results in the observed tapering for some NWs. NWs were released from the substrate by sonication in a 2-propanol solution and dispersed onto a *p*-type Si wafer with a 100 nm thick thermal oxide. Arrays of interdigitated Ti/Au (20 nm/300 nm) electrodes were patterned by optical lithography and annealed in vacuum for several minutes at 600° C, resulting in dozens of electrically contacted NW devices. A scanning electron microscopy image of two representative devices is shown in Fig. 1.

Figure 1. SEM image of patterned GaN NWs showing the metal contacts.

3. DEFECT SPECTROSCOPY OF GAN NANOWIRES

Despite the generally observed lack of TDs in GaN NWs, other point and extended defects are likely to degrade device performance and must be controlled to advance GaN NW technology. Insufficient understanding remains of the role and origin of deep level defects in GaN NWs. Looking to the large body of work concerning defects in thin film GaN provides limited guidance for interpreting defect activity in nanostructures. Compared to thin films, defects may incorporate differently in NWs due to the drastically different growth methods and the often more restrictive growth parameter space. The consequence and magnitude of defect activity can also vary strongly with NW size due to high surface area-to-volume ratio of NWs.

An additional complication to understanding the origin of defects in NWs is the lack of a deep level spectroscopy technique that is applicable to NWs, quantitative in defect state energy and density, and is able to determine the type of trapped carrier (electron versus hole). Capacitance-mode defect spectroscopy techniques such as deep level transient spectroscopy (DLTS) and photocapacitance are quantitative and widely employed to study deep level defects in thin film semiconductors. However, DLTS and photocapacitance are poorly suited to NWs because the miniscule NW depletion region area makes measurement of the absolute capacitance extremely challenging, requiring an elaborate experimental apparatus.

Luminescence methods are not subject to these size limitations and have been widely used to study deep levels in GaN NWs. However, a host of techniques including time-resolved luminescence, excitation power-dependent luminescence, temperature-dependent luminescence, and photoluminescence excitation (PLE) are required to extract the density and ionization energy of deep level defects. Furthermore, luminescence techniques are not well suited to study non-radiative deep level defects.

Figure 2. PC resonance of GaN NWs.

Photoconductivity (PC) has also been used to study defect states in GaN NWs, though quantitative deep level analysis via PC has yet to be demonstrated. The persistence and decay of *above-band gap* PC in GaN NWs has been explained in terms of surface defects and surface depletion effects without addressing the nature of specific band gap states.² Spectral photocurrent (SPC) investigations of GaN NWs emphasizing free carrier processes in the quasi-neutral NW region observed individual deep levels and interpreted the SPC spectra in a manner similar to luminescence,³ thus these investigations are subject to many of the aforementioned limitations of luminescence techniques.

In contrast previous PC studies of defects in GaN NWs that rely on free carrier generation, this work considers how space-charge effects alone can produce strong PC in NWs and thereby provide a quantitative method to study deep levels. For instance, majority carrier photoemission from a deep level in the surface depletion region of a NW increases the space-charge therein, which reduces w and increases the volume of the electrically conductive core to produce positive PC. Sub-band gap PC is then an attractive method to study defect states that are located in the NW surface depletion region, which can be a substantial portion of the NW volume. Thus we term this method depletion-mode PC to differentiate it from PC techniques that rely free carrier generation in NWs. In the development of this technique, we quantified the deep level defect energy and density in a GaN NW for the first time.

3.1. Interpreting Sub-bandgap Photoconductivity from GaN Nanowires

Electrical and optical measurements were conducted in atmosphere at room temperature. For steady-state PC scans, a 150 W Xe lamp broadband source was dispersed through a monochromator using appropriate mode sorting filters and proper slit widths to provide monochromatic illumination at 2 nm resolution, permitting photon energies of $2.0 \text{ eV} \leq h\nu \leq 3.6 \text{ eV}$ at 20 meV increments. The incident photon flux ranged between $\approx 5 - 50 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}$ across the spectrum. The NWs were illuminated for 120 s at each photon energy prior to collecting data, and PC spectra were taken with the sample held at fixed bias.

The absolute magnitude of the PC response ΔI relative to the dark current I_0 displayed in Fig. 2 evidences the dominance of depletion region processes for the sub-band gap PC of these NWs. All spectra were collected at $V = 1 \text{ V}$, except for NW B4, which was taken at $V = 0.5 \text{ V}$. Before considering the individual spectral features, the mechanism and interpretation of the PC behavior is discussed. Firstly, from the magnitude of ΔI due to sub-bandgap illumination, free carrier processes in the quasi-neutral region of the NWs can be ruled out as the main contributor to the steady-state PC response. For example, the total increase in the current of NW B4 due to sub-gap illumination $\Delta I = 0.95 \text{ } \mu\text{A}$ ($I_0 = 38.1 \text{ } \mu\text{A}$, $\Delta I/I_0 = 0.025$). Using the standard equation for photoconductivity for a thin device, $\Delta I = qFA t G \eta \alpha$, where q is the elementary charge, F is the photon flux, A is the device cross-sectional area, t is device thickness, G is the photoconductive gain, η is the quantum efficiency, and α is the absorption coefficient, the necessary G for $\Delta I = 0.95 \text{ } \mu\text{A}$ can be estimated. For the purpose of illustration, taking values of $F = 1 \times 10^{16} \text{ cm}^{-2}\text{s}^{-1}$, $A = 6 \times 10^{-9} \text{ cm}^2$, $t = 200 \text{ nm}$, $\eta = 1$, and $\alpha = 1 \times 10^4 \text{ cm}^{-1}$ yields $G \sim 5 \times 10^5$, which is unreasonably large and therefore discounts optical free carrier generation in the quasi-neutral region as the source of PC. Change in the contact resistance due to photoionization of metal-semiconductor states at the NW-Ti/Au interfaces facilitated by waveguiding of light under the

metal contacts is not a likely explanation for the PC response either. If the voltage drop at the contacts decreased significantly under illumination, a corresponding reduction in the “knee” voltage where ohmic transport gives over to SCLC transport should be observed.⁴ However, no such shift in the I - V data was observed under illumination (not shown). Therefore, we attribute the mechanism for the PC response of these NWs to a decrease in the surface depletion width due to deep level defect photoemission in the depleted regions, resulting in an increase in the cross-sectional area of the conductive, quasi-neutral region.

In such a model, PC arises not from generation of excess carriers due to deep level photoemission, but rather change in space-charge following deep level photoionization. Thus, the depletion-mode PC method applied here is more similar to photocapacitance than conventional PC. An important advantage of depletion-mode PC is that majority and minority carrier photoemission processes can be distinguished. For example, a majority carrier electron photoemitted from a deep level in the surface depletion region of an n -type NW will be swept to the quasi-neutral region, leaving behind an excess space-charge. This will cause the surface depletion layer to recede, increasing the conductive NW core and causing a positive PC response. Conversely, minority carrier hole photoemission will decrease the space-charge and increase the extent of the surface depletion region, causing a negative PC response. Thus, the sign of the inflection in the PC spectrum determines the type of photoemission process, which is an advantage over conventional PC methods, where both majority and minority carrier photoemission produces a positive PC change.

Recognizing the importance of depletion region processes in the PC response aids the interpretation of the individual PC spectral features. Similar to photocapacitance, deep level photoemission onsets are evident as inflection points in the PC spectra and denote the approximate defect energy level in the band gap. Since all the inflection points are positive in Fig. 2, the associated process is majority carrier (electron in this case) photoemission to the conduction band minimum E_c . Every spectrum displays similar thresholds at an average energy $h\nu = 2.23 \pm 0.05$ eV (except for NW F8), 2.54 ± 0.07 eV and 3.22 ± 0.02 eV, where the uncertainties are estimated from the deviations among these four samples. On the whole, the NW set with mean widths $\sim 100 - 200$ nm exhibited similar PC spectra features, though NW F8 lacked an onset at 2.23 eV and displayed reduced amplitude for the onset at 2.54 eV. A possible explanation for this discrepancy is that the NWs could have been located in removed regions of the growth substrate and subject to different temperatures during growth, leading to different preferential defect incorporation. Saturation of the PC signal was observed for $h\nu$ greater than the band gap energy of 3.44 eV.

The gradual increase in PC with increasing illumination energy following both the 2.23 eV and 2.54 eV onsets bespeaks lattice relaxation effects for the corresponding defect centers. The photoemission threshold of such a deep level is broadened and red-shifted by approximately the Franck-Condon energy compared to its classical optical ionization energy E_o due to phonon-assisted photoionization.⁵ Thus the actual location of these deep levels in the bandgap is likely deeper than 2.23 eV and 2.54 eV from E_c . Conversely, the 3.22 eV onset is sharp and does not indicate strong lattice coupling of the defect center, so it is reasonable to assign it at $E_c - 3.22$ eV in the band gap.

Figure 3. Calculated and measured PC response as a function of nanowire width.

Consistent with the depletion-mode PC model, the PC response tended to increase with decreasing mean NW width, which is also consistent with the reduction of dark conductivity with decreasing NW mean width observed in Fig. 2. Indeed, $\Delta I/I_0$ decreased by more than an order of magnitude for an approximate two-fold increase in the mean diameter of NW C5 compared to B4. Such an effect can be explained qualitatively as increasing impingement of the surface depletion region into the NW volume,² which enhances the depletion-PC response. To understand the dependence of deep level-stimulated PC of GaN NWs as a function of width in a more quantitative manner, an electrostatic model proposed for long, cylindrical NWs was adopted.² In this model, the radius of the conductive NW core r is related to the surface potential ϕ as

$$\phi = \frac{qN_d}{4\epsilon} \left[R^2 - r^2 \left(1 + 2 \ln \frac{R}{r} \right) \right] \quad (3.1)$$

where N_d is the ionized donor density, ϵ is the semiconductor permittivity, and R is the physical NW radius. Following previous studies of GaN NWs grown along the c -axis, ϕ was assumed to be 0.6 V and pinned at the surface Fermi level. The donor density can be estimated from the critical NW radius R_{crit} below which the NW is fully depleted,

$$N_d = \frac{4\epsilon\phi}{qR_{crit}^2} \quad (3.2)$$

A previous study of NWs grown under similar conditions as the NWs in this work determined a critical mean width ~ 100 nm.⁶ Taking $R_{crit} = 50$ nm yields $N_d = 4.83 \times 10^{17} \text{ cm}^{-3}$. Using these values, Eq. (3.1) was solved numerically for $r(R)$. To simulate the PC response to deep level photoemission, a deep level density N_t was assumed to be 3% of N_d . The conductive core radius

under illumination $r'(R)$ was re-calculated assuming full photoionization of deep levels in the depletion region resulting in an effective donor density $N_d' = N_d + N_t = 4.97 \times 10^{17} \text{ cm}^{-3}$. Assuming an abrupt transition between the depleted and quasi-neutral zones of the NW and that sub-band gap illumination produces negligible changes in n and the electron mobility, $\Delta I/I_0(R)$ is approximately equal to $(r'/r)^2 - 1$. The results of the calculation are shown in Fig. 3, where it is found that $(r'/r)^2 - 1$ and therefore $\Delta I/I_0$ increase rapidly as r approaches R_{crit} . Overlaid on the calculation are the data from the present study, demonstrating good agreement between the model and experiment. The closeness of the fit is likely fortuitous considering the greatly simplified NW geometry of the model and neglect of the different facets of the actual NWs. Nevertheless, the general trend of strongly increasing $\Delta I/I_0$ with decreasing NW width, as anticipated in the depletion-mode PC model, is borne out. More generally, this analysis also indicates that, for conductive NWs with geometries that are well approximated by a long cylinder and with reliable values of N_d and ϕ pinned by the Fermi level, the calculation described here could be used to determine N_t in NWs.

It is useful to compare the GaN NW deep level PC spectra to previous reports of GaN planar films. Many previous photocurrent and photocapacitance studies of planar GaN films grown by a variety methods report broad thresholds in the range of 2.54 – 2.67 eV^{7,8,9,10,11,12,13} and sharper onsets in the range of 3.22 – 3.3 eV,^{8,11,12,13,14,33,34} similar to the NW deep level spectra reported here. As photocapacitance has poor sensitivity to surface states, and the bandgap states in the photocurrent studies of Refs. 12 and 13 were ascribed to bulk defects, the similarities among the bulk GaN spectra of these previous investigations and the NW spectra observed in this study strongly suggest that the NW defects corresponding to the 2.54 eV threshold and $E_c - 3.22$ eV level are related to defects that pervade the NW volume and are not particular to the NW surface. Such a compelling comparison to planar GaN films has not been found for the 2.23 eV NW onset, so its relation to either a bulk or surface defect remains speculative.

The microscopic origin of the 2.54 eV onset is now considered. Steady-state photocapacitance investigation of GaN films grown by MOCVD at 76 torr for enhanced carbon incorporation¹⁵ and films grown by MBE with direct carbon doping,¹⁶ exhibited a broad deep level threshold at 2.54 eV, similar to that observed in the GaN NW. Attributing the 2.54 eV onset to carbon impurities agrees with our previous investigation of GaN NWs⁶ grown under similar conditions in the same reactor, which proposed that, based on correlated reduction in the intensity of the yellow luminescence band and resistivity, carbon incorporation is likely in these NWs.

The physical origin of the defects producing the 2.23 eV and 3.22 eV deep level onsets are more speculative, though threading dislocations can be ruled out because NWs grown under these conditions are observed not to contain threading dislocations. The absence of the $E_c - 3.22$ eV level in n -type GaN thin films grown by MBE⁹ suggests the potential role of an impurity that is more prominent in MOCVD growth rather than a native defect species, while a complex including both intrinsic and extrinsic defects is possible.

In summary, the deep level spectra of UID, n -type GaN NWs grown by the VLS method via MOCVD were investigated using depletion-mode PC, where the PC response was consistent with changes in the surface depletion width rather than free carrier excitation in the quasi-neutral region. Dominant deep level thresholds at 2.23 eV and 2.54 eV and a deep level at $E_c - 3.22$ eV

were observed and attributed to majority carrier photoemission. A simple model was used to explain the observed increase of photoconductivity with decreasing NW width. The NW deep level spectral features were similar to n -type bulk GaN films, suggesting that the NW deep levels pervade the NW volume and are not particular to the surface.

3.2. Deep level optical spectroscopy of GaN Nanowires

While steady-state PC enabled calculation of NW defect density and gave some indication of the energy levels of the observed defects, we implemented a depletion-mode PC adaptation of deep level optical spectroscopy¹⁷ (DLOS) to measure the absolute optical ionization energy (E_o) and Franck-Condon shift (d_{FC}) of defect states in GaN NWs. Hence, DLOS enables quantitative comparison of NW deep level spectra to the more extensive and better understood deep level spectra of thin film GaN. Combined with micro-photoluminescence (μ -PL), DLOS provides important insight into the possible physical origin of the corresponding defects. First, a detailed description of the modeling approach for simulations of DLOS on NWs is presented, followed by the experimental DLOS and μ -PL data. The results are compared to existing reports in the literature for defects in bulk GaN, and the origin of the observed NW defects are considered.

DLOS measurements were conducted at room temperature. For DLOS scans, light from a 150 W Xe arc lamp broadband source was dispersed through a monochromator using appropriate mode sorting filters and proper slit widths to provide monochromatic illumination at 2 nm resolution, permitting a photon scan from 1.2 eV to 3.6 eV at 25 meV increments. The incident photon flux ϕ range was between $\approx 5 - 20 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}$ across the spectrum. DLOS was conducted at fixed bias of $V = 0.25 \text{ V}$ for both NWs, corresponding to an approximate applied electric field $V/L = 1780 \text{ V/cm}$ and 850 V/cm for NWs E5 and E6, respectively, where L is the NW length spanning the electrical contacts. The NWs were illuminated for 70 s at a given energy, and DLOS transients were measured using a current preamplifier and sampled at 500 μs intervals with an oscilloscope. A 30 s dark quiescent period followed every DLOS transient to allow the PC to decay.

DLOS is a method to isolate the majority (or minority) carrier optical emission rate of a deep level. By measuring the spectral dependence of the majority carrier optical emission rate, the deep level optical cross-section $\sigma(h\nu)$ can be determined. Fitting the spectral dependence of σ to an appropriate theoretical model^{17,18} determines the value for E_o and d_{FC} (when appropriate). To demonstrate the applicability of DLOS to NWs, it is useful to first review its implementation to thin film semiconductors.

In general, during illumination of an n -type semiconductor containing a deep level with a negligible thermal emission rate and density N_t , the occupied deep level density n_t in the depletion region is¹⁹

$$n_t(t) = \frac{e_p}{e_n + e_p} N_t - \left[\frac{e_p}{e_n + e_p} N_t - n_t(0) \right] \exp[-(e_n + e_p)t] \quad (3.3)$$

where $e_{n(p)}$ is the optical emission rate of electrons (holes), and illumination begins at $t = 0$. For $h\nu$ greater than half of the band gap, the net optical emission rate is a sum of e_n and e_p . However, to determine E_o , either e_n or e_p must be isolated. When the deep level is fully occupied initially, i.e. $n_t(0) = N_t$, it can be shown that¹⁷

$$\left. \frac{dn_t}{dt} \right|_{t=0} = -e_n N_t \quad (3.4)$$

A complimentary expression can be derived for hole photoemission.¹⁷ Equation (2.4) is fundamental to DLOS as a photocapacitance technique applied to thin films.¹⁷ For a depletion region formed at a planar interface, the initial rate of change of the photocapacitance ΔC is proportional to (dn_t/dt) .²⁰ Then, following Eq. (3.4),

$$d(\Delta C)/dt|_{t=0} \propto e_n \quad (3.5)$$

and the spectral dependence of the deep level optical cross-section $\sigma_n = e_n/\phi$ is thus determined.

Application of DLOS, a photocapacitance technique intended for planar depletion regions, to PC measurements of a NW with a triangular surface depletion region is not obvious and is established here. To validate the experimental approach, the remainder of this section describes the modeling and numerical simulation of how the sub-band gap PC change (ΔI) relative to the dark value (I_0) depends on deep level photoemission in the NW surface depletion region. It is shown using numerical simulations that $d(\Delta I)/dt|_{t=0}$ is proportion to e_n , similar to Eq. (3.5), and the differential PC spectra of NWs accurately reflect the spectral dependence of e_n .

Space-charge effects, and not free carrier effects, dominate the sub-band gap PC for NWs with a physical radius (R) that is comparable to w . In GaN NWs at equilibrium, it is expected that Fermi level pinning at the NW surface produces a space-charge, resulting in a surface depletion region that restricts the electrically conductive volume of the NW. Sub-band gap illumination can stimulate deep level photoemission in the surface depletion region and change w . For instance, majority carrier photoemission from a deep level in the surface depletion region of a NW increases the space-charge therein. The resulting decrease in w corresponds to an increase of the cross-sectional area of the conductive, quasi-neutral NW core (A_σ) and produces a positive PC transient. Conversely, minority carrier photoemission produces a negative PC transient. The dominance of electron or hole photoemission is thus determined for NWs of known conductivity type. This PC mechanism is more akin to photocapacitance than it is to either typical PC²¹ or photocurrent²² of bulk films due to the pivotal sensitivity of PC to changes in w rather than changes in n . Contributions to the sub-band gap PC due to free carrier effects are negligible. Efficient thermal re-capture of free carriers quenches deep level photoemission in the quasi-neutral NW core. Further, sub-band gap illumination is not expected to change the electrical mobility of free carriers in the NW. Therefore, ΔI is proportional to ΔA_σ .

To apply DLOS to NWs, a relation between n_t and ΔA_σ must be found to demonstrate that e_n is proportional to $d(\Delta A_\sigma)/dt|_{t=0}$, similar to Eq. (3.5). For the case of a long, cylindrical NW, the following relation for the surface potential (Φ) can be derived,²³

$$\Phi = \frac{q(N_D - n_i)}{4\varepsilon} \left[R^2 - r^2 \left(1 + 2 \ln \frac{R}{r} \right) \right] \quad (3.6)$$

where q is the elementary electric charge, N_D is the shallow donor density, r is the radius of the conductive NW core, and ε is the semiconductor permittivity. Since $r = \sqrt{A_\sigma/\pi}$, Eq. (3.6) contains A_σ and n_i , however, n_i cannot be algebraically related to r using Eq. (3.6). Thus, numerical calculations for a cylindrical NW were carried out to determine the functional dependence of $A_\sigma(t)$ as $n_i(t)$ changes in the depletion region during illumination. Though the actual geometry of the NW devices studied in this work is triangular, the calculations still provide useful insight to the interpretation of the experimental PC transients.

Simulations of $\Delta A_\sigma(t) \propto \Delta I(t)$ under illumination indicated that the PC response of the NW due to deep level photoemission in the surface depletion region is mono-exponential. For these simulations, Eq. (3.3) was used to describe $n_i(t)$ in Eq. (3.6), and it is through Eq. (3.3) that e_n and e_p enter the calculation. Since isolating e_n and e_p is most difficult experimentally when they have similar magnitudes, the arbitrary conditions $e_n = 0.75 \text{ s}^{-1}$ and $e_p = 0.5 \text{ s}^{-1}$ were simulated. The absolute magnitudes of e_n and e_p are unimportant; only their relative values affect the results of the simulation. A dilute defect density was assumed, *i.e.* $N_i/N_D = 0.05$. Using Eqs. (2.3) and (2.6), $r(t)$ was solved self-consistently for a NW of $R = 155 \text{ nm}$ with $n_i(0) = N_i$ and an equilibrium $N_D = 4.8 \times 10^{17} \text{ cm}^{-3}$. The latter value is consistent with previously investigated UID GaN NWs. Following previous studies of GaN NWs grown along the a -axis, Φ was assumed to be 0.6 V and pinned at the equilibrium surface Fermi level.² Simulated values of $A_\sigma(t)$ were then obtained at time intervals of 10 ms as deep level emission proceeds. The natural log of $[A_\sigma(\infty) - A_\sigma(t)]$ demonstrated linear behavior, indicating exponential decay. A least-squares fit of $A_\sigma(t)$ to mono-exponential decay (not shown) yielded an emission rate $e_T = 1.27 \text{ s}^{-1}$ for the simulated PC transient. Thus, the transient behavior of $A_\sigma(t)$ is exponential with an emission rate that is approximately $(e_n + e_p) = 1.25 \text{ s}^{-1}$, as might be expected from Eq. (3.3). The rates e_n and e_p can vary greatly with respect to each other as $h\nu$ is scanned during DLOS, so $e_n/e_p = 2, 4$, and 10 were also simulated at fixed $e_p = 0.5 \text{ s}^{-1}$. Agreement within 2% was found between e_T and $(e_n + e_p)$ for each e_n value.

Figure 4. Nanowire PC transient fitted as a monoexponential decay.

Having established that depletion-mode PC response of a NW is exponential, the proportionality between $d(\Delta A_\sigma)/dt|_{t=0}$ and e_n was investigated. Simulations of $d(\Delta A_\sigma)/dt|_{t=0}$, [calculated by taking a linear regression of ΔA_σ over the range $t = 0 - (0.1/e_T)$] were well fit by a line, confirming that the simulated values for $d(\Delta A_\sigma)/dt|_{t=0}$ are approximately proportional to e_n . Thus, the equation

$$\left. \frac{d(\Delta I)}{dt} \right|_{t=0} \propto e_n \quad (3.7)$$

can be used to measure the spectral dependence of $\sigma_n = e_n/\phi$. The upshot of these considerations is that if $N_t \ll N_D$, then the PC transient of a cylindrical NW due to deep level photoemission in the surface depletion region is expected to be exponential of the form of Eq. (3.3) and amenable to DLOS analysis using Eq. (3.7).

In light of these simulated results, it is anticipated that the photoemission transients of triangular NWs are exponential and appropriate for DLOS when $N_t \ll N_D$. For experimental verification, the recorded PC transient from NW E6 under 2.46 eV illumination and a least-squares fit to exponential decay are shown in Fig. 4. The inset shows the linearized exponential fit. The actual NW transient is indeed well described by an exponential, suggesting that N_t/N_D is small for these NWs and that DLOS analysis is justified both physically and mathematically for the present investigation.

Considering now the spectral dependence of the NW PC, three PC onsets due to deep level defect photoemission are evident in both spectra near 1.6 eV, 2.5 eV, and 3.2 eV, and saturation occurs at the band gap $E_g = 3.44$ eV. Unlike traditional PC measurements of bulk films, saturation rather than an onset occurs in the PC spectrum at the E_g because the PC response is dominated by Δw as Δn is negligible. Similar to photocapacitance, changes in the NW surface

depletion region saturate for $h\nu \geq E_g$ as defect absorption begins to compete with band-to-band absorption.

Figure 5. DLOS of GaN nanowires.

Positive ΔI_{SS} indicates majority carrier photoemission, so these PC onsets are attributed to deep level photoemission to the conduction band minimum, E_c , for these n -type NWs. The PC thresholds near 1.6 eV and 2.5 eV are rather broad, suggesting strong lattice coupling and large d_{FC} for the corresponding defect centers.²⁴ For such a case, the PC onset can be significantly red-shifted compared to E_o . Hence, DLOS analysis was used to determine E_o . The σ_n spectra determined from DLOS for both NWs are shown in Fig. 5. It is emphasized that the DLOS spectra reflect the change in the *electron photoemission rate* with $h\nu$ and do not indicate the magnitude of $\Delta I/I_o$. The spectra are similar except for variations in the onset energies. These differences are not significant though, since it is the spectral dependence, rather than the onset energy, of σ_n that is fundamental to the defect center. Values of $E_o = 1.77$ eV ($d_{FC} = 0.78$ eV) and 2.81 eV ($d_{FC} = 0.28$ eV) were extracted, respectively, from fitting the data to the model of Chantre *et al.*¹⁷ As anticipated for these deep levels, the PC onset energy is red-shifted compared to E_o , which is consistent with the sizeable d_{FC} . Conversely, the onset near 3.2 eV is abrupt and can be described by the model of Lucovsky,¹⁸ which does not involve significant lattice relaxation, yielding $E_o = 3.19$ eV. As previously discussed, the E_o values are referenced to E_c .

The μ -PL spectrum for NW E6 is shown in Fig. 6, and NW E5 exhibited similar PL features. The spectrum was modeled with a least-squares fit to Gaussian peaks. The main features are broad deep level bands peaked at 2.19 eV, 2.38 eV, and 2.74 eV, and a band edge peak at 3.40 eV. The present study is concerned with comparing the μ -PL and DLOS spectra to better understand the physical origin of the defects.

Figure 6. GaN NW mPL.

The NW DLOS spectra in Fig. 5 are similar to deep level spectra reported for thin film GaN. Photoionization current spectroscopy of MOCVD-grown GaN metal-semiconductor field effect transistor devices containing a highly resistive GaN:C buffer layer revealed a deep level with $E_o = 2.85$ ($d_{FC} = 0.25$ eV) reported by Klein *et al.*²⁵ that was found to correlate with carbon incorporation.²⁶ These energies are similar to the $E_c - 2.81$ ($d_{FC} = 0.28$ eV) deep level observed here. The energetic position in the band gap of the $E_c - 2.81$ eV NW deep level is also similar to a band gap state at $E_c - 3.0$ eV ($d_{FC} = 0.4$ eV) revealed by photocapacitance-mode DLOS of carbon-doped GaN thin films grown by MBE,²⁷ whose defect concentration was also found to track carbon doping.²⁷ Thus, carbon is considered to be a likely source for $E_c - 2.81$ eV NW deep level given its close comparison to carbon-related deep levels found in GaN:C thin films.^{25,26,27} Previous work on NWs grown under similar conditions concluded that NW electrical conductivity was critically sensitive to carbon incorporation,⁶ further corroborating the role of carbon as a deep level defect in these NWs. However, other potential defect level defects such as the gallium vacancy (V_{Ga}) cannot be conclusively ruled out.²⁸ Room-temperature PLE measurements of UID thin film GaN revealed absorption spectra ranging from 2.6 – 3.2 eV²⁸ that were similar to the DLOS spectrum of the $E_c - 2.81$ eV deep level observed here but were attributed to electron photoemission from a V_{Ga} -related defect. However, the reported 3.32 eV peak energy and 0.52 eV full width at half maximum of a Gaussian fit to the PLE spectra in Ref. 28 implies a defect level that is deeper in the band gap and is subject to stronger phonon coupling than the $E_c - 2.81$ eV NW deep level. Therefore, carbon seems to be a more likely source than V_{Ga} for the $E_c - 2.81$ eV NW band gap state.

The NW μ -PL spectrum is also comparable to those reported for bulk GaN and corroborates the existence of carbon-related defects in the NWs. The dominant 2.19 eV band has similar peak energy to PL bands widely reported for both UID GaN thin films²⁸ and UID NWs⁶ as well as GaN:C thin films.^{29,30,31} Since the 2.19 eV band dominates the NW μ -PL spectrum, it is expected that the corresponding defect should also produce a strong feature in the DLOS spectrum. The most likely candidate is the $E_c - 2.81$ eV level. The discrepancy between the 2.19 eV peak energy of the PL band and the 2.81 eV optical ionization energy can be reconciled within a one-

dimensional configuration-coordinate (1D-CC) model.²⁴ Within the 1D-CC model, $E_o - d_{FC}^{abs} = E_{pk} + d_{FC}^{em}$, where d_{FC}^{abs} denotes the Franck-Condon energy associated with photon absorption (as in DLOS), E_{pk} is the peak energy of the luminescence band, and d_{FC}^{em} is the Franck-Condon energy associated with photon emission. Ideally, d_{FC}^{em} would be determined from temperature-dependent PL measurements, and the relation between the 2.19 eV PL band and the 2.81 eV DLOS feature could be shown to be self-consistent within the 1D-CC model. In the absence of temperature-dependent PL measurements, a value $d_{FC}^{em} = E_o - d_{FC}^{abs} - E_{pk} = 0.34$ eV can be calculated. A large body of precedent work on thin film GaN establishing a correlation between carbon doping and a) the intensification of a luminescence band centered near 2.2 eV^{29,30,31} and b) increasing N_t of a deep level with a photoionization energy of 2.85 - 3.0 eV^{25,25,27} provides additional support for the association of the 2.19 eV μ -PL band and the $E_c - 2.81$ eV deep level in the present study to the same carbon-related defect. However, as mentioned earlier, other deep level defects such as V_{Ga} cannot be conclusively ruled out as sources for the $E_c - 2.81$ eV deep level and the 2.19 eV μ -PL band.²⁸

Figure 7. (a). SEM image showing the triangular cross-section of a GaN nanowire; (b)-(e) monochromatic CL images of the same nanowire at 366 nm, 428 nm, 566 nm, and 734 nm; (f). composite image of (b) and (d).

Regarding the $E_c - 1.77$ eV ($d_{FC} = 0.78$ eV) NW deep level, this band gap state is also similar to an $E_o = 1.8$ eV ($d_{FC} = 0.6$ eV) deep level reported for GaN:C thin films grown by MOCVD.²⁵ However, extended defects such as threading dislocations, rather than carbon, were proposed as a possible source for 1.8 eV deep level in thin film GaN:C.²⁶ The lack of a deep level near $E_c - 1.8$ eV in MBE-grown GaN:C films²⁷ is consistent with a source other than carbon for this bandgap state. However, since these GaN NWs are free of threading dislocations, another defect must give rise to the $E_c - 1.77$ eV band gap state. Further investigation is required to ascertain the microstructure of the $E_c - 1.77$ eV defect level, though its similarity to defect states reported in bulk GaN discount surface-related defects.

Relations among the 2.37 eV and 2.74 eV μ -PL bands and the deep levels observed via DLOS are not evident. The similar peak energy and relatively low intensity of the 2.37 eV band compared to the 2.19 eV band suggests that the deep levels have similar positions in the band gap and that the DLOS spectra of the latter defect center overwhelms that of the former. The

broadness of the 2.74 eV band indicates that the corresponding defect center undergoes a large lattice relaxation upon photoionization.²⁸ Thus, the DLOS spectrum of the associated defect is also expected to be very broad with an E_o that is hundreds of meV greater than 2.74 eV due large d_{FC}^{abs} and d_{FC}^{em} . This picture is not compatible with the DLOS spectrum of the $E_c - 3.19$ eV state that exhibits no d_{FC}^{abs} . Since no deep levels observed via DLOS are attributable to the 2.74 eV band, the DLOS spectra of this deep level likely overwhelmed by the $E_c - 2.81$ eV and $E_c - 3.19$ eV levels.

The $E_c - 3.19$ eV DLOS feature of the NW device is characteristic of MOCVD-grown n -type GaN thin films^{32,33,34} and NWs and is attributed to photoemission from a discrete band gap state. The close agreement between the $E_o = 3.19$ eV DLOS spectrum in the current investigation for a NW and previous reports of a band gap state 3.22 – 3.25 eV below E_c in n -type thin film GaN^{32,33,34} strongly suggest that the 3.2 eV onset is due to photoemission from a discrete deep level. The $E_c - 3.19$ eV level itself is not expected to be strongly affected by the FKE due to greater localization of the trapped carrier compared to a free carrier.³⁵

Despite the many reports of a deep level near $E_c - 3.2$ eV in n -type GaN grown by a variety of methods,^{32,33,34} the physical origin of this deep level remains speculative. In light of the present investigation, threading dislocations can be ruled out because NWs grown under similar conditions are not observed to contain threading dislocations. Since the $E_c - 3.19$ eV band gap state observed here and in other GaN NWs appears to be the same as reported for GaN thin films,^{32,33,34} defects exclusive to the NW surface can be confidently ruled out as well.

In summary, the deep level spectra of UID, n -type GaN NWs grown by the VLS method via MOCVD were investigated using DLOS and μ -PL. Simulations demonstrated that DLOS analysis is appropriate for NWs with $N_t \ll N_D$ when the extent of the surface depletion region controls the PC response due to deep level photoemission. Deep levels were observed using DLOS at $E_c - 1.77$ eV ($d_{FC} = 0.78$ eV), $E_c - 2.81$ eV ($d_{FC} = 0.28$ eV), and $E_c - 3.19$ eV, and μ -PL revealed a dominant deep level band centered at 2.19 eV. DLOS enabled quantitative comparison between the NW deep levels and those reported for thin film GaN. The resemblance of DLOS and luminescence spectra to previous reports of bulk GaN suggests that the NW deep levels are not particular to the surface. The $E_c - 2.81$ eV band gap state is possibly carbon-related due to its similarity to the dominant deep level in GaN:C thin films. It is suggested that the $E_c - 2.81$ eV state and the 2.19 eV μ -PL band correspond to the same carbon-related defect.

3.3. Cathodoluminescence of GaN Nanowires

While DLOS provides significant insight into the physics of defects in GaN NWs, spatial distribution of the point defects in GaN nanowires has not been fully established. In particular, a link of the yellow luminescence (YL) near 560 nm with surface states in GaN thin films¹⁹ and bulk materials²⁰ has been previously suggested, which could have significant implications for GaN nanowires given their high surface-to-bulk ratio. In addition, previous studies on the dependence of the electrical and optical characteristics on the nanowire dimensions suggest a nonhomogenous distribution of defects in the GaN nanowire.^{15-16, 21} To further elucidate nature of defects in GaN nanowires, we present here a detailed study on the spatial distribution of defect-related luminescence in GaN nanowires using spatially-resolved cathodoluminescence

(CL) imaging and spectroscopy. CL can achieve much higher resolutions compared to other optical probe techniques such as micro-photoluminescence (better than 20 nm spatial resolution have been recently reported using a scanning transmission electron microscopy based CL setup)²², which is of particular importance in studying nanostructures.

A representative SEM image of a GaN nanowire with exposed cross-section is shown in Fig. 7(a). CL spectra of the nanowire were taken showing emission peaks centered around 366 nm (band-edge luminescence, BEL), 428 nm (blue luminescence, BL), 566 nm (YL), and 734 nm (red luminescence, RL). Monochromatic CL images were subsequently acquired from the same nanowire at these four wavelengths and are shown in Fig. 7 (b)-(e). In Fig. 7 (b), intense BEL (366 nm) is seen at the nanowire cross section as expected. A monochromatic CL image taken at the center of the blue luminescence (BL) band at 428 nm is shown in Fig. 7(c), where the 428 nm emission is seen to distribute fairly uniformly over the cross-section of the nanowire. This result suggests that the BL related defects are uniformly distributed in the nanowire. In dramatic contrast to the BEL and BL, the YL at 566 nm is observed to be highly localized near the surface of the GaN nanowire as shown in Fig. 7(d).

From the 566 nm CL image, YL surface layer thicknesses of ~80 nm and ~60 nm are measured on two different facets, which may possibly be related to the different {1-101} and {0001} facets of the nanowire. The thickness of the surface YL on the third facet cannot be measured as it cannot be resolved from the YL from the nanowire sidewall. The thickness of the surface YL layer was defined as FWHM of the CL intensity profile. In the bulk region of the nanowire, the monochromatic CL image at 566 nm appears relatively dark; however, the YL intensity near the center of cross section of the nanowire is non-zero. We observed a relatively weak YL intensity using the spot mode CL, which will be discussed in the following section, and which indicates weaker YL originating from the nanowire bulk. An additional defect related emission at 734 nm corresponding to the red luminescence (RL) band in GaN, is also observed and has a uniform distribution in the nanowire bulk, as shown in Fig. 7(e).

Interestingly, we note that the 566 nm monochromatic CL image (Fig. 7 (d)) shows an elevated background (YL outside the nanowire) as compared with the other monochromatic CL images. We believe this elevated YL background may result from the strong YL surface component on the GaN nanowires. When the impinging electron beam scans to a location adjacent to a nanowire, some scattered electrons impact the nearby GaN nanowire surface. These reduced-energy, scattered electrons primarily excite the surface region of the GaN nanowire, which leads to a YL background signal in the image. The indium/Si substrate was verified as not being the source of the background YL by scanning an area distant from any nanowires. We also note that the observed CL intensities of the BEL appear higher in the lower left corner/edge of the nanowire, but not for the BL. The exact origin of the observed BEL intensity variation in the nanowire cross-section has not yet been determined, although it could possibly be due to the presence and distribution of nonradiative defects,^{7, 29} which as a competing carrier recombination pathway could locally reduce BEL. The lower observed CL intensity at the left edge of the nanowire is likely an edge effect whereby the electron beam interaction volume is reduced by the concave interior angle.

Figure 8. (a). A monochromatic CL image obtained at 566 nm of a GaN nanowire. (b). CL spectra acquired while focusing the electron beam at various locations on the nanowire cross-section as shown in (a).

The spatial dependence of the nanowire optical emissions was further investigated by taking CL spectra while focusing the electron beam at designated locations across a nanowire cross-section. Fig. 8(a) shows a 566-nm monochromatic CL image of a nanowire, where a ~100 nm thick YL surface layer is clearly observed. When the electron beam is focused at the outer edge of this surface YL layer (Spot 1), strong YL is seen to dominate the CL spectrum while the BEL near 366 nm is barely detectable (Spectrum a, Fig. 8(b)). As the electron beam is moved to the center region of the surface YL layer (Spot b), the height of the BEL peak is estimated to increase by ~3 times while the YL intensity remains roughly constant (Spectrum b). When the electron beam is focused at the inner edge of the surface YL layer (Spot c), the BL & RL peaks appear and the BEL intensity continues to increase, while the YL intensity still remains roughly constant. As the electron beam is targeted at the center of the nanowire (Spot d), the BL, RL, and BEL peak intensities saturate while the YL decreases dramatically, but does not go to zero (Spectrum d). This non-zero YL intensity was further confirmed at the centers of larger nanowires with

dimensions (widths) on the order of 1 μm . We therefore rule out the possibility that the YL detected in the bulk (core) is caused by excitation of the surface YL layer because the nanowire dimension is larger than electron energy dissipation volume ($\sim 0.32 \mu\text{m}$ diameter) of the excitation beam, as estimated using a Monte Carlo simulation. The data from Fig. 7 and Fig. 8 thus indicates that the BEL, BL, and RL emission is absent from the surface region exhibiting strong YL. This indicates that the defects giving rise to BL and RL are not surface-related, and also that BEL is quenched in the YL surface region of the nanowire.

Figure 9. (a) SEM image showing a tapered GaN nanowire. The scale bar is 0.5 μm . (b) and (c) The corresponding monochromatic CL images at 366 nm and 566 nm. (d). Spot-mode CL spectra obtained along the center line of the nanowire are plotted as a function of the nanowire dimension (width).

We measured a critical distance d_c as a nanowire dimension when the surface YL completely “pinches off” the BEL by studying a tapered GaN nanowire, the shape of which results from competing nanowire sidewall growth. The SEM image in Fig. 9(a) represents a typical tapered nanowire and its monochromatic CL images for BEL and YL are given in Fig. 9(b) and (c), respectively. A salient feature is that when the dimension of the nanowire is less than $\sim 170 \text{ nm}$ the BEL is below the detection limit whereas YL can be clearly seen as the nanowire diameter decreases below 170 nm. By moving the electron beam along the center line of the nanowire axis, we obtained a series of CL spectra (Fig. 9(d)) as a function of the nanowire dimension. These spectra confirmed that the BEL can no longer be detected as the dimension of the nanowire decreases below d_c , which in this case is estimated to be $\sim 175 \text{ nm}$. Based on the geometry of an equilateral triangle, a close approximation of our nanowire geometry, a surface YL thickness that corresponds to this d_c is $\sim 50 \text{ nm}$. Above the critical nanowire dimension, BEL

and BL intensities are seen in Fig. 9(d) to increase with increasing nanowire diameter (and hence increasing volume probed) up to ~300 nm, where the dissipation volume becomes the limiting factor. YL can also be observed at the catalyst tip region in Fig. 9(c), which is the likely result of GaN surrounding the catalyst as confirmed through energy dispersive x-ray mapping.

Point defects may be incorporated into the nanowire through the vapor-liquid-solid (VLS) growth mechanism at the Ni catalyst tips or through the competing lateral (“sidewall”) growth on the nanowire side walls. The nanowire surface itself may also be a source of defects (e.g. dangling bonds). In Fig. 9, the nanowire region directly below the Ni catalyst tip has a diameter of approximately 60 nm and can be assumed to be primarily comprised of VLS-grown “core” material rather than sidewall-growth material, since the axial VLS growth rate is substantially faster than the radial sidewall growth rate. Although this tip region is seen to be dominated by YL in Fig. 9, it is difficult to determine whether this is a result of YL related defects being incorporated through the VLS growth mechanism (e.g. catalyst tip) or by YL resulting from surface dangling bonds combined with the finite resolution of the technique. We propose that the YL-related defects may initially form or incorporate through sidewall growth or a combination of sidewall and VLS (catalyst) growth, and then subsequently redistribute toward the surface during nanowire growth via a diffusion-related mechanism. Isolated gallium vacancies (V_{Ga}), which have been linked to YL,¹¹ were reported to become mobile at 500-600 K with an estimated migration energy of 1.5 eV³⁰, and thus represent a potential defect source for the surface-related YL. The weaker bulk related YL may arise from other less-mobile defects linked to YL, such as C and O impurities,¹¹ or from the same defects responsible for the surface YL (e.g. V_{Ga}) but at lower concentrations.

BL and RL are observed to be fairly evenly distributed in the nanowire bulk without a distinct surface component, which suggests that the BL and RL related defects may be relatively stable and do not migrate towards the surface during growth. Potential candidates for the BL related defect include V_{Ga} -related complexes, specifically $V_{\text{Ga}}\text{-O}_\text{N}$.³¹⁻³² which has been reported to have a relatively high diffusion barrier of 2.2 eV^{30, 33}, and thus may be relatively immobile. The RL band is less common and less studied in GaN than the YL and BL bands.¹¹ In GaN thin films, RL was reported in carbon-doped GaN and attributed to have an origin from threading dislocations.³⁴⁻³⁵ However, since these GaN nanowires are free of threading dislocations,¹⁷ a different type of defect must be considered in this case. Hofmann et al. observed a RL at 1.8 eV in MBE grown GaN and suggested that $V_{\text{Ga}}\text{-O}_\text{N}$ or $V_{\text{Ga}}\text{-Si}_\text{Ga}$ could be responsible for the RL.³⁶ Since the nanowires in this study were not intentionally doped with Si, the $V_{\text{Ga}}\text{-Si}_\text{Ga}$ complex is unlikely to represent the source of the RL here. These complexes are also expected to be relatively immobile, consistent with our hypothesis. Regardless of their respective origins, the absence of surface-related BEL, BL, and RL indicates that YL dominates the other radiative recombinative pathways in the surface region.

In summary, defect-related luminescence in GaN nanowires was investigated using spatially-resolved CL. The results reveal the presence of a strong YL (566 nm) surface layer and a much weaker YL component in the nanowire bulk. In contrast, BEL at 366 nm and other defect-related luminescence at 428 nm (BL) and 734 nm (RL) are observed only in the nanowire bulk and not at the surface, where YL dominates. As the nanowire dimension decreases to a critical dimension the nanowire is pinched-off by the high-defect-density surface layer, entirely

quenching BEL. The strong surface-related YL layer may be caused by the diffusion and piling up of mobile point defects, such as Ga vacancies, at the surface during growth. Since surface scatter of phonons is expected to impede thermal conductivity of nanowires, preferential defect migration to near-surface regions is expected to play a role in the thermal budget and breakdown mechanism of GaN nanowire devices.

4. THEORETICAL MODELING OF THERMAL TRANSPORT IN GAN NANOWIRES

Thermal conducting properties of semiconductor nanostructures e.g., nanowires has been actively explored in recent years because they directly impact many important applications including microelectronics and thermoelectrics. In the microelectronics application, a continuous decrease in feature sizes has resulted in a continuous increase in heat generation. This trend has placed an increasingly demanding requirement for the semiconductor materials to have a high thermal conductivity to effectively dissipate the excessive heat to the surrounding environment. In the thermoelectrics application, on the other hand, a low thermal conductivity is desired because it results in an increase in the energy conversion efficiency. At the nanometer length scale, the effective thermal conductivity becomes sensitive to feature dimensions and defect concentrations. While this provides an effective means to tailor thermal conductivity for specific applications, the scaling of thermal conductivity against feature dimension is not always clear. Because experimental measurement of thermal conductivity is increasingly more challenging as the feature size decreases, a theoretical understanding of thermal conductivity as a function dimension can play a critical role towards optimizing many nanostructure applications including microelectronics and thermoelectrics.

When an accurate interatomic potential is available, the use of molecular dynamics (MD) simulations in studying the thermal transport properties of crystals may become desired. This is because the computational system used in MD simulations captures exactly the lattice nature of the crystal, which enables effects of surfaces and defects to be accurately incorporated. It has been shown that a reasonably accurate determination of thermal conductivity requires a real time of MD simulation for at least tens of nanoseconds. At this time scale, the system size that can be effectively employed usually contains no more than a million of atoms even with massively parallelized MD simulations. For GaN, this translates to about 10^4 nm^3 of material volume. However, the GaN nanowires grown in experiments can have radius exceeding 20 nm and length exceeding 20 μm . This corresponds approximately to a material volume exceeding 10^7 nm^3 . As a result, significant length-scale difference exists between the simulated and the real systems. Even with rather small systems, MD simulations have been relatively successfully applied to determine thermal conductivities of bulk materials based upon either the Green-Kubo and its variations³⁶ or the “direct method.”³⁷ In the Green-Kubo method, periodic boundary conditions are used in all the three coordinate directions. As was demonstrated in previous work and will be reexamined in the following, the use of periodic boundary conditions effectively extends the dimension of a small computational system to infinity. As a result, an infinitely large bulk crystal can be well captured with the Green-Kubo method even when a small simulated system is used. In the direct method, periodic boundary conditions can also be applied in the two coordinate directions perpendicular to the heat flux so that these two directions can be viewed as infinity. However, the direct method involves a heat source and heat sink along the heat conducting direction. A finite spacing, L , must be imposed between the source and the sink. Fortunately, both experiments and theories indicated that the inverse of thermal conductivity $1/\kappa$ and the inverse of length scale $1/L$ satisfy accurately a linear scaling relationship,

$$\frac{1}{\kappa} = \frac{1}{\kappa_b} + \frac{\alpha}{L} \quad (4.1)$$

where κ_b is the bulk thermal conductivity at $L \rightarrow \infty$, and α is a dimension-independent coefficient. To obtain bulk thermal conductivity, several simulations for different small cell lengths are performed, and the results can then be relatively accurately extrapolated to the infinite-size limit due to the linearity of the relationship. Periodic boundary conditions cannot be used for finite system dimensions. However, if a reliable linear scaling law that is applicable from nano up to macro scales is known, the thermal conductivity of finite systems at realistic length scales can still be accurately predicted based upon data obtained from MD simulations on a nano scale. An underlying assumption of Eq. (4.1) is that the two dimensions perpendicular to the heat flux are infinite. Because of this, Eq. (4.1) is essentially a scaling law for 2D films where the heat flux is through the film thickness L . Unfortunately, no similar scaling laws were previously available for other heat flux directions (e.g., parallel to the film surface) or other nanostructures (e.g., nanowire or nanoparticles). As a result, previous MD simulations had not been applied to calculate thermal conductivities at realistic length scales for many interesting nanostructures, including cases where heat conduction occurs in the plane of a film or through the axis of a wire. We developed a theoretical scaling law that defines thermal conductivity of a nanostructure as a function of all of its three independent dimensions: thickness t , width W , and length L :

$$\begin{aligned} \kappa(t, W, L) = & \frac{L \cdot \kappa_{0,c}}{L + \delta_0} - \left[\frac{L \cdot \kappa_{0,c}}{L + \delta_0} - \frac{L \cdot \kappa_{1,c}}{L + \delta_1} \right] \cdot \left(\frac{2d}{t} + \frac{2d}{W} \right) \\ & + \left[\frac{L \cdot \kappa_{0,c}}{L + \delta_0} + \frac{L \cdot \kappa_{2,c}}{L + \delta_2} - 2 \cdot \frac{L \cdot \kappa_{1,c}}{L + \delta_1} \right] \cdot \frac{4d^2}{t \cdot W} \end{aligned} \quad (4.2)$$

Where $\kappa_{0,c}$, $\kappa_{1,c}$, $\kappa_{2,c}$, δ_0 , δ_1 , δ_2 and d are seven constants that can in principle be determined from available thermal conductivity vs. dimension data. By performing very large MD simulations at different system dimensions, we have demonstrated that Eq. (4.2) is highly accurate from nanoscales all the way to macroscopic scales. The development of such an analytical scaling law has begun to enable MD simulations to be used to predict thermalconductivity of nanostructures at realistic length scales.

The goal of the present work is threefold. First, we provide more detailed physics of the scaling law by adapting it for general 2D film and 1D wire cases. Next, we explore the conditions and parameter space under which the scaling law can be accurately applied, and discuss the methods to predict thermal conductivity of nanostructures at realistic length scales. Finally, we perform large scale MD simulations to determine the [0001] thermal conductivities of a wurtzite GaN crystal constructed in two nanostructure configurations: (i) (1-100) film with varying film thickness and (ii) a [0001] hexagonal wire with varying wire radius. GaN is chosen for the case study because it has excellent optoelectronic properties and can be easily integrated with the existing silicon structures. In addition, some GaN applications, such as laser diodes and high electron mobility transistors operate at high current and power densities. Understanding thermal transport of GaN nanostructures helps these applications, especially for device breakdown issues.

Figure 10. Heat conduction through the length L of a box-shaped material with a thickness t and a width W .

The underlying assumption of our scaling law is accurate when the dimension of the structure is larger than the phonon mean free path. For GaN bulk crystals, the phonon mean free path has been estimated to be approximately 50 nm at 300 K and 10 nm at 500 K from both experimental data and kinetic theory. In nanostructures, the apparent mean free path is reduced due to surface scattering, reducing the thermal conductivity. Interestingly, for given cross section, simple theoretical analysis indicated that the inverse of the phonon mean free path along the length direction is a linear function of inverse of the length. This suggests that the inverse of the thermal conductivity is also a linear function of the inverse of the length, matching exactly the prediction of the scaling law. This means that the scaling law can actually be applied even when the length scale is comparable with the phonon mean free path. We will re-examine this in the following. Our theory can be extended and applied to arbitrary heat flux directions with respect to arbitrary shapes of the nanostructure. Here we confine our discussion to thin film and nanowire cases.

4.1 Thin Film Case

The geometry of the film case is illustrated in Fig. 10(a) where heat is assumed to flow through a finite length L of a box-shaped sample with a finite thickness t and an infinite width $W \rightarrow \infty$. Note that for a true 2D film, $L \rightarrow \infty$. A more general scenario of finite L is assumed here so that the theory can be applied with the direct method MD simulations where a finite spacing between heat source and heat sink must be used. It is recognized that the size-effect on thermal conductivity origins from the surface scattering of phonons. Hence, we separately consider surface and bulk regions of the sample. As shown in Fig. 10(a), the sample is divided along the thickness direction into three smaller box-shaped regions (referred to as plates hereafter): the inner (core) plate has a thickness of $t - 2d$ and is marked as “0” because it does not bound any y-

surfaces, and the two outer (shell) plates have a thickness d and are designated as “1” because they bound one y - surface. When the thickness t is very large, we can always choose a sufficiently large shell thickness d so that the thermal transport behavior of plate 0 is independent of the presence of the top and the bottom free surfaces that are far away. This means that the thermal conductivity of plate 0 is independent of t and therefore can be expressed as a function of L only: $\kappa_0(L)$. The local thermal conductivity inside plate 1 is non-uniform near the surface. However, plate 1 still exhibits an apparent overall thermal conductivity. Note that at a large d , there is really no “distinguishable” interface between plates 0 and 1 as the thermal transport properties from both sides of the interface approach the same bulk values. This means that once a large value of d is given, the apparent thermal conductivity of plate 1 can also be expressed as a function of L only: $\kappa_1(L)$.

Using Fig. 10(a), we assume that the left hand side of the sample is kept at a high temperature of T_h and the right hand side at a low temperature of T_l . Because the vertical temperature gradient is zero at the “indistinguishable” interface between plates 0 and 1, we can list separately the thermal transport equations for the two types of plates:

$$\kappa_0(L) = \frac{J_0}{\frac{T_h - T_l}{L}} \quad (4.3)$$

$$\kappa_1(L) = \frac{J_1}{\frac{T_h - T_l}{t}} \quad (3.4)$$

where J_0 and J_1 are, respectively, the heat fluxes through plates 0 and plate 1. Note that because of an assumed zero vertical temperature gradient at the 0/1 interface, the high and low temperatures are the same for both types of plates. The overall thermal conductivity of the system is expressed as

$$\kappa = \frac{J}{\frac{T_h - T_l}{L}} \quad (4.5)$$

where the total flux J can be calculated as an area-weighted average

$$J = \frac{W \cdot (t - 2d) \cdot J_0 + 2W \cdot d \cdot J_1}{W \cdot t} = \frac{(t - 2d) \cdot J_0 + 2d \cdot J_1}{t} \quad (4.6)$$

as in parallel conductors. Substituting Eqs. (4.3), (4.4), and (4.6) into Eq. (4.5), we have

$$\kappa(t, L) = \kappa_0(L) - [\kappa_0(L) - \kappa_1(L)] \cdot \frac{2d}{t} \quad (4.7)$$

Now we consider the thermal transport through the i -th plate ($i = 0, 1$). Imagine that the plate is divided along the length direction into three sections: the center section contains a length of $L - 2\omega$ and is marked as “ c ”, and the two end sections contain a length of ω and are marked as “ e ”, as shown in Fig. 10(b). Just as a subsurface thickness d subsumes the scattering of the side surfaces, a subsurface length ω subsumes the scattering of the end surfaces (including the artificial effects of the thermostats). Here we distinguish d and ω for generality. It can be seen

that for a given large value of ω , which is always possible when L is sufficiently large, the thermal transport behavior of the center section is independent of the presence of the two end surfaces that are far away. This means that the apparent thermal conductivity of the center section is equal to a constant $\kappa_{i,c}$ ($i = 0, 1$). In particular, $\kappa_{0,c}$ corresponds to the bulk thermal conductivity κ_b by definition. Similar to the discussion in the above, the apparent thermal conductivity exhibited by the two end sections is also independent of L and therefore is equal to another constant $\kappa_{i,e}$. Because heat flows through the three sections of the plate in serial, the heat flux J is a constant. We can list the temperature difference between the left and right ends as:

$$T_h - T_l = \frac{J}{\kappa_{i,c}} \cdot (L - 2\omega) + \frac{J}{\kappa_{i,e}} \cdot (2\omega) \quad (4.8)$$

The inverse of the overall thermal conductivity of the plate, $\kappa_i^{-1}(L)$, equals $J^{-1} \cdot (T_h - T_l)/L$. We can therefore write:

$$\kappa_i(L) = \frac{L \cdot \kappa_{i,c}}{L + \delta_i} \quad (4.9)$$

where

$$\delta_i = 2\omega \cdot \frac{\kappa_{i,c} - \kappa_{i,e}}{\kappa_{i,e}} \quad (4.10)$$

δ_i combines the relative change of thermal conductivities between the center and the end sections with the length ω , it therefore reduces one parameter. This reduction in parameters is expected because ω and $\kappa_{i,e}$ are dependent. It can be seen from Eq. (4.10) that δ_i can be viewed as a characteristic length measuring the scattering of the end surfaces. Substituting Eq. (4.9) into Eq. (4.7), we have a scaling law for the thin film:

$$\kappa(t, L) = \frac{L \cdot \kappa_{0,c}}{L + \delta_0} - \left[\frac{L \cdot \kappa_{0,c}}{L + \delta_0} - \frac{L \cdot \kappa_{1,c}}{L + \delta_1} \right] \cdot \frac{2d}{t} \quad (4.11)$$

Eq. (4.11) involves five parameters: $\kappa_{0,c}$, $\kappa_{1,c}$, δ_0 , δ_1 , and d . These five parameters have physical meanings and must be subject to some physical constraints. First, the surface thickness d and the associated surface thermal conductivity $\kappa_{l,c}$ are dependent parameters. Hence, d can be selected and only the corresponding $\kappa_{l,c}$ value be treated as an unknown parameter. However, d is not completely arbitrary as it must be large enough to subsume the surface scattering effect. Once d is large enough, Eq. (4.11) can always predict accurate results regardless of its particular value for any film thickness t that satisfies the geometry condition $t > 2d$. On the other hand, a large d prevents Eq. (4.11) from being used for small thickness t due to the constraint $t > 2d$. So it is important to understand the lower bound of d . Clearly d is sufficiently big if it equals the phonon mean free path in the bulk crystal. As described above, this might be overly stringent.

Figure 11. Heat conduction through a finite length L of a circular wire with a finite radius r .

Once d is chosen, the remaining parameters can be fitted to the available data. For MD applications, it is necessary to perform several simulations at different dimensions in order to fit Eq. (4.11). Note that if the minimum system thickness used in these simulations is t_{min} , then the largest d that still enables all the MD data to satisfy the geometry condition is $t_{min}/2$. In order to find a small d to enable study of small structures, a trial-and-error approach can be used. For instance, d can be first set to $t_{min}/2$, and Eq. (4.11) fitted to all MD data. If satisfactory fitting is obtained as will be described below, then the selected d is good. Otherwise d can be set according to the next thinnest sample, and the thinnest (t_{min}) sample is disqualified from the fitting. This process is continued until an appropriate d is found. There are also some useful relations. Because the end section is assumed to have more surface scattering than the center section, and plate 1 has surface scattering that is assumed to be insignificant in plate 0, we always have $\delta_i > 0$ ($i = 0, 1$), $\kappa_{l,c} < \kappa_{0,c}$, and $\kappa_l(L) < \kappa_0(L)$ (for any L). These conditions are automatically satisfied during fitting provided that the data to be fit are accurate and d satisfies the geometry constraint.

Eq. (4.11) can be used for infinite 2D films. When $t \rightarrow \infty$, the problem is essentially the heat conduction through the length L of a film (L is in fact the “thickness” in this case). When $L \rightarrow \infty$, Eq. (4.11) gives thermal conductivity in the plane of a film as a function of the film thickness t . In addition, Eq. (4.11) can also be used for quasi- 2D cases or even 1D cases, e.g. out-of-plane conduction, to explore the dimensional effects by using different t/L ratios.

4.2 Nanowire Case

The wire case is illustrated in Fig. 11, where heat is assumed to flow through the length L of a circular sample with a finite radius r . Using the same theory described above, the sample is divided along radius direction into an inner, smaller cylindrical core with a radius of $r - d$ and an outer cylindrical shell with a thickness of d . The core does not bound any free surfaces whereas the shell terminates with a radial surface, and hence the core and shell are denoted as “0” and “1” respectively. It can be seen that when r is very large, we can always choose a sufficiently large d to subsume the surface scattering effect so that the thermal conductivities of the core and the shell are independent of the wire radius and hence can be expressed as functions of L using $\kappa_0(L)$

and $\kappa_l(L)$ respectively. In Fig. 11, we again assume that the sample is held at a high temperature of T_h at the left and a low temperature of T_l at the right. The thermal transport equations for the core, shell and overall system can be represented by Eqs. (4.3) - (4.5). The total flux J , however, is modified as

$$J = \frac{J_0 \cdot \pi \cdot (r - d)^2 + J_1 \cdot [\pi \cdot r^2 - \pi \cdot (r - d)^2]}{\pi \cdot r^2} \quad (4.12)$$

After appropriate substitution from prior equations, one finds

$$\kappa(r, L) = \frac{L \cdot \kappa_{0,c}}{L + \delta_0} - \left(\frac{L \cdot \kappa_{0,c}}{L + \delta_0} - \frac{L \cdot \kappa_{1,c}}{L + \delta_1} \right) \cdot \left(\frac{2d}{r} - \frac{d^2}{r^2} \right) \quad (4.13)$$

Eq. (4.13) reduces to Eq. (4.1) when $r \rightarrow \infty$, and it matches Eq. (4.2) using the geometry conditions of a circular wire: $t = W = 2r$, $\kappa_{2,c} = \kappa_{l,c}$, and $\delta_l = \delta_2$. Eq. (4.13) involves the same five parameters as in the film case. The geometry of the wire case, however, requires that $d < r$. For MD applications, the maximum d enabling all MD data equals the minimum radius $r_{\min}$ used in the series of MD simulations. With d determined similarly as in the film case, the remaining four parameters can be fitted to the measurements. Done correctly, the parameters satisfy $\delta_i > 0$ ($i = 0, 1$), $\kappa_{l,c} < \kappa_{0,c}$, and $\kappa_l(L) < \kappa_0(L)$ (for any L).

Eq. (4.13) has numerous uses. When $L \rightarrow \infty$, Eq. (4.13) represents thermal conductivity through an infinite 1D wire as a function of wire radius. In particular, Eq. (4.13) indicates that thermal conductivity of wires is a linear function of $2d/r - d^2/r^2$. When r is large, the thermal conductivity increases to a first order with $\sim -1/r$, in agreement with the approximate equation derived by Lu *et al.* from the Boltzmann equation. Eq. (4.13) can also be used in other cases. For instance, at $r \rightarrow \infty$, the problem reduces to heat conduction through the thickness L of an infinite 2D film. It can be used for quasi-2D films or even 3D particles to explore the dimension effects by using different r/L ratios.

4.3 Molecular Dynamics Methods

One ultimate goal of our work is to enable MD simulations to predict thermal conductivities of GaN films and wires at realistic, device length scales on the order of 100 nm or more, which is not at bulk limit but too long to directly simulate with MD. Here we describe details of the interatomic potential used in the MD, the computational cells for film and wire configurations, and the thermal transport simulation method. We used applied the Stillinger-Weber (SW) potential parameterized by Bere and Serra³⁸ to calculate the thermal conductivity of GaN bulk crystals. This potential gives reasonable prediction on dispersion relations, vibrational density of states (DOS), and heat capacity for bulk systems.

The computational system used for the film simulations is shown in Fig. 12, where the color scheme shows the temperature (red means the highest temperature and blue means the lowest temperature). Similar to Fig. 10, we assume that the sample has a finite thickness t in the y -direction and an infinite width $W \rightarrow \infty$ in the z -direction. Following the customary approach with

the direct method MD simulations, a periodic boundary condition was used in the x - direction. As will be shown below, this means that the system dimension in the x -direction is $2L$ rather than L .

Figure 12. Atomistic configuration for film MD simulations.

The equilibrium GaN has a wurtzite hexagonal crystal structure. The hexagonal crystal has three orthogonal directions $[0001]$, $[-1100]$, and $[11-20]$. To study thermal conduction along the $[0001]$ direction of a low energy (-1100) film, the computational supercell is aligned so that the x -, y -, and z -coordinates correspond respectively to $[0001]$, $[-1100]$, and $[11-20]$ directions. The experimental lattice constants of the hexagonal wurtzite are $a = 0.319$ nm, $c = 0.519$ nm, and internal displacement between Ga and N sublattices $u = 0.377$. With the SW interatomic potential used here, the zero temperature lattice constants are $a = 0.319$ nm, $c = 0.520$ nm, and $u = 0.375$. Converting the hexagonal crystal to the smallest orthogonal unit cell, the lattice constants of the unit cell are respectively $a_1 = c = 0.520$ nm, $a_2 = 2 \cdot a \cdot \cos(\pi/6) = 0.55252$ nm, and $a_3 = a = 0.3190$ Å in the x -, y -, and z -directions. For convenience, the system dimension can be represented by the number of cells n_1 , n_2 and n_3 in the x -, y -, and z -directions. In addition to the difference in unit, n_1 , n_2 and n_3 always refer to the simulated size whereas t , W and L refer to the real size that can become infinite.

Two series of sample dimensions, one corresponding to $n_1 = 100$ and the other one corresponding to $n_1 = 150$, were studied at various n_2 ranging from 50 to 150 and in addition at $t \rightarrow \infty$ using a fixed $n_3 = 5$. The film scenario with the (-1100) film surfaces was simulated using a free boundary condition in the y -direction with surfaces terminated between the larger spacing as will be described in details in the wire case. Such a termination ensures stable surfaces and therefore no surface reconstruction was observed in simulations. The $t \rightarrow \infty$ or $W \rightarrow \infty$ case was simulated by using a periodic boundary condition in the corresponding direction. Note that although the periodic boundary condition is also used in the x -direction, the meaningful dimension in the x -direction for the direct method MD simulations is the spacing between heat

source and heat sink. This spacing is not extended by the periodic boundary condition and is always finite.

Figure 13. Atomistic configuration for wire MD simulations black and white colors distinguish Ga and N atoms, and the star shows the center of the wire cross-section.

Unlike the circular wire assumed in Fig. 11, the GaN wires observed in experiments are often hexagonal with $\{0001\}$ axis and $\{-1100\}$ facets. The computational system used for simulations of such wires is shown in Fig. 13(a). The crystal orientations are the same as those used for the film simulations, except that atoms beyond specified $\{-1100\}$ surfaces are removed. As in Fig. 11, the system is assumed to have a finite radius r , which is defined as the minimum distance between the center of the wire and the surface, Fig. 13(b). Again the system dimension in the x -direction is assumed to be $2L$ rather than L to facilitate the periodic boundary condition.

The cross section of the hexagonal wire is examined in details in Fig. 13(b). It can be seen that the $\{-1100\}$ atomic planes have two different spacings. We found that if the surface is terminated between the small spacing, such as that shown by the dash line, then the surface is composed of many dangling bonds resulting in high energy and unstable configurations. Hence, the surfaces of our wires are always terminated between the large spacing. It can also be seen that the smallest repeatable spacing of the $\{-1100\}$ planes is $a_r = a \cdot \cos(\pi/6) = 0.27616$ nm. For convenience, the system dimension in the x - and the radial directions can be respectively represented by number of cells n_l and n_r (in unit of a_r). A matrix of dimensions with the

longitudinal dimension n_l ranging from 100 to 300 and the radial dimension n_r ranging from 4 to 12 was explored. Here free boundary conditions were used in the y - and z - directions and the periodic boundary condition used in the x -direction.

The thermal transport MD simulations were performed under a constant number of atoms, constant system volume, and constant system energy (NVE) condition using a time 14step size of $\Delta t = 1$ fs. To accurately account for the effect of thermal expansion and eliminate the errors due to statistical fluctuation of the simulated temperature, the following steps were used to create the initial crystal. First, a crystal was created by assigning atom positions according to the prescribed crystal lattice and the known lattice constants at zero temperature. A molecular dynamics simulation in the constant atom number, (zero) pressure, and temperature (NPT) ensemble was subsequently performed for a total of 20 ps period. The desired simulated temperature was achieved using the velocity rescaling method. After discarding the first 10 ps simulation to allow the system to reach a steady state, the average crystal sizes and average total (kinetic and potential) system energy were then calculated for the remaining 10 ps. We then created another crystal using the average sizes obtained at the finite temperature. We can also calculate the potential energy of this newly created crystal by simply performing an energy calculation simulation. The difference between the average total system energy obtained from the NPT run and the potential energy of this crystal prescribes exactly the amount of the kinetic energy that needs to be added in order for this crystal to exhibit the same total average energy over the subsequent long constant energy thermal transport simulation. We added precisely this amount of kinetic energy into the system by first assigning velocities to atoms according to Boltzmann distribution and then rescaling the velocities under the zero total linear momentum condition.

The thermal transport simulation is started immediately without the conventional long NPT or NVT simulation to establish the initial temperature. The advantage of this approach is that once steady-state is reached, the average temperature of the system matches exactly the desired temperature. In practice, we found that the difference between the average temperature in the middle of the heat source and heat sink (where the thermalconductivity was calculated) and the desired temperature is well below 1 K (often near 0.01 K or less). It is more general because the initial crystal is not required to be in the minimum potential energy configuration, which may not be easily determined when the system includes surfaces.

The direct method requires the creation of a heat source and a heat sink. As shown in Fig. 12, the heat source corresponds to the red region at the far left of the cell, and the heat sink is the blue region near the middle of the cell. During simulations, the size and location of the source and sink regions are specified. With appropriate choices of system length, source and sink region width, and locations of different regions, we ensured that the source and sink regions were geometrically identical, and that the left side of the sink (or source) region was exactly symmetric to its right side, up to another source (or sink) region (which may be its periodic image). Here the width of the source or sink region is around 4 nm. It can be seen from Fig. 12 that the heat source at the left side has an image at the right side under the periodic boundary condition in the x -direction. Consequently, even the length of our system is $2L$, the spacing between the source and the sink is still L as shown in Fig. 10.

Figure 14. Thermal-conductivity data obtained for wire at 500 K, $d = 11.05$ Å.

The constant flux method³⁹ was used to create the temperature gradient. In this method, a constant amount of energy is added to the hot region and exactly the same amount of energy is removed from the cold region at each MD time step using velocity rescaling (while preserving linear momentum). To ensure that the high and the low temperatures are reasonable and consistent in different runs, the heat flux has been adjusted within 0.00035 to 0.0010 eV/(ps·Å²) to give a consistent high-low temperature difference (say 5 - 10 K). To generate extremely accurate results, the first 0.4 ns simulation was discarded to allow the system to reach a steady state, and the remaining duration of simulations was chosen to be at least 11 ns and many reached over 20 ns. To compute the temperature profile, the system dimension in the x -direction is divided into a grid. The temperature of each of the grid cells was averaged over the remaining time of simulations. The temperature profile and the input heat flux were used to calculate the thermal conductivity using Fourier's Law, Eq. (4.5). To estimate the statistical error of the calculated thermal conductivity, the total averaging time was divided into 20 subsections and thermal resistivity (or conductivity) was calculated for each of the subsections.

It should be noted that under the periodic boundary condition in the x -direction, the observed dependence of thermal conductivity upon the system length L comes primarily from the scattering of the interfaces at the hot and the cold regions. The functional dependence on L can still be well described by Eqs. (4.11) and (4.13), albeit δ_i should be viewed as an interface scattering parameter rather than surface scattering parameter. Because our analysis extrapolates the MD data to an $L \rightarrow \infty$ limit (i.e., true film and true wire), the interface approximation will not affect the results.

MD simulations we performed to study thermal transport for wires at 500 K. Only one temperature is studied due to the expense of the calculations. 500 K was chosen because it is likely to be above the Debye temperature. To deduce all the parameters, simulations were carried out using a matrix of three sample length of $2L \approx 520$ Å ($n_l = 100$), 1040 Å ($n_l = 200$), and 1560 Å ($n_l = 300$) and four sample radius of $r \approx 11$ Å ($n_r = 4$), 16 Å ($n_r = 6$), 22 Å ($n_r = 8$), and 33 Å ($n_r = 12$). Eq. (4.13) indicates that at a given length L , κ is a linear function of $2d/r - (d/r)^2$ and at a given radius r , $1/\kappa$ is approximately a linear function of $1/L$.

Figure 15. Thermal-conductivity data obtained for wire at 500 K, $d = 22.09$ Å.

Here we explore two different chosen d values, $d = 11.05$ Å and $d = 22.09$ Å. Using $d = 11.05$ Å (which is the largest d that enables all MD data to satisfy the geometry condition of the scaling model), κ vs. $2d/r - (d/r)^2$ curves at different L are shown in Fig. 14(a) and $1/\kappa$ vs. $1/L$ curves at different r are shown in Fig. 14(b). In addition, the κ values obtained at infinite cross-section dimension (i.e., $r \rightarrow \infty$) obtained in the previous work⁴⁰ are included in Fig. 14. In Fig. 14, the lines are calculated using Eq. (4.13). It can be seen that Fig. 14 exhibits some linear relationships predicted by Eq. (4.13). However, the overall match between the MD data and the model prediction is not great. Most seriously, Fig. 14(a) indicates that a linear regression using merely the data points at large $2d/r - (d/r)^2$ values would not closely extrapolate to the data point at $2d/r - (d/r)^2 = 0$ (i.e., $r \rightarrow \infty$), and Fig. 14(b) shows significant deviation of the predicted curves from the data points.

To improve the results, we explored an alternative method by again using the scaling theory. Film simulations described in the previous section resulted in the determination of five parameters $\kappa_{0,c}$, $\kappa_{l,c}$, δ_0 , δ_l , and d . These five parameters have physical meanings and are invariant in the wire configurations. As a result, we can directly use these parameters and Eq. (4.13) to calculate wire thermal conductivity. Some results of this calculations at a few different radii $r \geq d = 138.13$ Å are included in Fig. 15(b) using stars. It can be seen that although the predicted results from film simulations using large $d = 138$ Å and wire simulations using small $d = 22.09$ Å are different, the difference is relatively small at least for GaN. Note that while the film parameters based upon large $d = 138$ Å give better results, they cannot be used to calculate thermal conductivity at $r < d = 138$ Å. For true wires, we set $L \rightarrow \infty$. The film parameters and Eq. (4.13) were used to predict wire thermal conductivity as a function of radius. The results are shown in Fig. 16.

Figure 16. Predicted thermal conductivity of wire as a function of wire radius.

We have explored general scaling equations that explicitly express thermal conductivity of film and wire as functions of dimensions. Based upon these scaling equations, we have demonstrated methods that enable molecular dynamics simulations to be used to predict thermal conductivity of nanostructures at realistic length scales. We have performed extensive MD calculations of thermal conducting properties along the [0001] direction of GaN films and wires. The following conclusions have been obtained:

- The linear relationships predicted from the scaling equations hold extremely well for MD data at a large parameter d . Reliable prediction of film thermal conductivity as a function of film thickness has been achieved using linear interpolation.
- Thermal flux in nanostructures exhibit a clear difference between the surface and core whereas temperature is nearly constant across the cross-section, thereby verifying the core-shell assumption of the scaling theory and the near-zero heat flux perpendicular to the axis connecting hot and cold reservoirs.
- Due to the limitation of computational cost, parameters deduced from direct MD simulations of wires may not sufficiently accurately predict the wire thermal conductivity at large wire radii. However, the parameters deduced from film simulations enable the derivation of a reliable expression of wire thermal conductivity as a function of wire radius.
- The simulated dimension does not affect the thermal conductivity when the dimension is transverse to the heat flow and a periodic boundary condition is used in that direction. Hence, the periodic boundary conditions can be used to accurately extend the system dimension to infinity.

5. MECHANISM FOR ELECTRICAL BREAKDOWN IN GAN NANOWIRES: INFLUENCE OF THERMAL PROPERTIES AND DEFECTS

Particularly attractive device applications include vertically oriented nanoscale laser diodes (LDs) and high electron mobility transistors (HEMTs). Both LDs and HEMTs however operate at high current and power densities, and thus heat dissipation in the active device regions requires careful consideration. Recent experimental and theoretical studies on Si nanowires indicate that as the nanowire diameter decreases below approximately 150 nm, the thermal conductivity is reduced due to phonon surface scattering thus raising further concerns about heat dissipation. In this work we use the position and intensity of band edge μ -PL to deduce the temperature profile along individually contacted and resistively heated GaN nanowires resting on Si/SiO₂ substrates. By comparing measured μ -PL spectra from individual nanowires subjected to various levels of Joule heating with spectra calculated based on a one-dimensional heat transport model, we estimate the nanowire's thermal conductivity κ and the thermal conductance G''_{nw-sub} between the nanowire and the Si/SiO₂ substrate as 55 ± 25 W/m K and 56 ± 5 W/mm² K, respectively (G''_{nw-sub} is the inverse of nanowire-substrate thermal resistance per unit area which includes thermal resistance due to the material interface as well as heat spreading within the substrate). Least-squares fits to data indicate that such estimates for thermal conductivity and nanowire-substrate thermal conductance are relatively insensitive to the values of other parameters, which account for effects such as the finite temperature rise of the nanowire at its endpoints and the thermal quenching of μ -PL spectra with increasing temperature. Our results show that for long nanowires heat is dissipated primarily into the Si/SiO₂ substrate resulting in nearly flat temperature profiles that are ideal for estimating nanowire-substrate thermal conductance G''_{nw-sub} but which lead to high uncertainty in estimating nanowire κ . We find that some nanowires can sustain a dc power above 100 mW, and that catastrophic failure occurs at an average current density of approximately 3×10^6 A/cm² and at estimated peak temperatures less than 1100 K. The nanowire breakdown temperature and the observed morphology at the failure region, indicate that nanowire failure is the result of GaN thermal decomposition and is in good agreement with decomposition studies⁴¹ conducted on bulk GaN. We also report direct observation of thermal decomposition of GaN nanowires using transmission electron microscopy, achieved by Joule heating several nanowires to failure inside a transmission electron microscope (TEM) specially designed for in-situ electrical characterization. TEM images clearly show the formation and growth of Ga balls (i.e. Ostwald ripening) leading to eventual nanowire failure. Observation of thermal decomposition of GaN nanowires with TEM not only confirms the failure mechanism but also provides a second method to estimate the nanowire's thermal conductivity because the input power and temperature dependence of GaN thermal decomposition are approximately known. We find that estimates for nanowire thermal conductivity based thermal decomposition are in good agreement with those obtained using μ -PL spectroscopy second method to estimate the nanowire's thermal conductivity because the input power and temperature dependence of GaN thermal decomposition are approximately known. We find that estimates for nanowire thermal conductivity based thermal decomposition are in good agreement with those obtained using μ -PL spectroscopy.

5.1 Determination of GaN Nanowire Thermal Conductivity

A He-Cd laser focused through a 32 $\times$ reflective objective and a CCD camera /spectrometer combination coupled to the electrical probe station microscope were used to record the μ -PL spectra for each nanowire. The resulting laser spot on the sample had a diameter of approximately 10 μ m and a total continuous wave power of 1 mW. A band pass filter was used to minimize reflected laser light from reaching the CCD camera or the spectrometer. A schematic of the experimental set-up is shown in Fig. 17a.

Figure 17. (a) Experimental set-up; (b) PL spectra collected at six levels of applied power. Insets show PL images of the nanowire collected with the same camera settings at 0 and 3.6 mW. (c) FESEM images of the nanowire after failure.

To heat the nanowires, a dc bias was applied in steps of 1 V, and sufficient time was allowed to ensure that steady state conditions were achieved at each step. This process was repeated until nanowire failure, as evidenced by an open circuit. At each voltage step several μ -PL spectra were recorded to estimate the temperature of the nanowire. A total of 10 nanowires were tested in this manner, and an additional 5 nanowires were tested to failure by increasing the voltage at a rate of 0.25 V/sec without recording μ -PL spectra. One of the nanowires was mounted on a substrate heater and was heated isothermally while its μ -PL data was collected in order to calibrate the μ -PL system. After failure, the nanowires were examined in a field emission scanning electron microscope (FESEM) to determine the location and morphology of the failure region and the dimensions of each specimen.

Figure 17b contains μ -PL band edge spectra collected for one of the nanowires at increasing power settings and shows that as more power is supplied to the nanowire, the band edge luminescence (BEL) peak decreases in intensity (thermal quenching), broadens, and red shifts to lower energies. The insets in Fig. 17b illustrate the effects of thermal quenching on the μ -PL intensity. The images were collected under identical camera settings (zero auto gain control) at 0 mW and 3.6 mW applied power. At 0 mW applied power the wire has relatively uniform brightness; however, when heated, the middle section of the nanowire becomes noticeably dimmer than the edges. This phenomenon is due to the fact that the middle section of the nanowire is at a higher temperature than the edges, and thus Arrhenius quenching of the μ -PL signal reduces the brightness. Broadening and red shifting of the BEL spectra with increasing power are discussed below. Increasing the applied power above 3.6 mW resulted in nanowire failure. Subsequently, the nanowire was characterized by FESEM and a representative image is shown in Fig. 17c.

It is apparent that the temperature profile of the nanowire featured in Fig. 17 is nonuniform, and therefore a thermal model of the nanowire is needed to interpret the μ -PL data and assess device performance. Such a model is developed below. First, however, we consider BEL spectra from an isothermal GaN specimen, which can be approximated as a Gaussian function of the photon energy E_{phot}

$$I_{PL}(E_{phot}, T) \Big|_{T=const.} = \frac{I_0}{\sqrt{2\pi}\sigma(T)} \exp\left[\frac{-E_A}{k_B T}\right] \exp\left[\frac{-(E_{phot} - E_G(T))^2}{2\sigma(T)^2}\right] \quad (5.1)$$

$I_{PL}(E_{phot}, T)$ is the PL intensity at a specified photon energy and temperature, and I_0 represents the BEL intensity at 0 K. The temperature dependence of the intensity comes from three terms: (a) an exponential term to account for Arrhenius quenching of the (integrated) intensity with increasing temperature, (b) the decrease of the band gap energy $E_G(T)$ with increasing temperature effecting a shift of the peak intensity, and (c) the standard deviation of the Gaussian function $\sigma(T)$ herein referred to as the peak width, which accounts for thermal spreading of the spectrum.

The temperature dependence of the band gap is modeled by the well-known Varshni Equation:

$$E_G(T) = E_G \Big|_{T=0K} - \frac{\alpha \cdot T^2}{T + \beta} \quad (5.2)$$

where $\alpha = 0.909$ meV/K, $\beta = 830$ K, and the band gap $E_G(T) = 3.507$ eV at 0 K. The peak width $\sigma(T)$ of PL spectra obtained from GaN samples increases with temperature and for temperatures greater than 300 K is well approximated as a linear function $\sigma(T) = \sigma_{300K} + \sigma_T(T - 300 \text{ K})$ with empirical coefficients σ_{300K} and σ_T .

For nanowires with non-uniform temperature profiles, such as those in powered devices, the BEL peak position cannot be used directly with Eq. (5.1) to estimate the temperature of the

nanowire. Rather, the μ -PL spectrum acquired at the full field detector must be treated as a convolution of spectra originating from regions of the nanowire at different temperatures. Assuming that the temperature profile $T(x)$ of the nanowire is approximately one-dimensional, the total μ -PL spectrum takes the form of an integral over the nanowire's length L :

$$I_{PL}(E_{phot}) = \frac{1}{L} \int_0^L I_{PL}(E_{phot}, T(x)) dx \quad (5.3)$$

Equation (5.3) represents an implicit relationship between the temperature profile of a nanowire and its measured μ -PL spectrum. A comparison between calculated and observed spectra provides a means for validating heat flow simulations and estimating values for parameters such as the nanowire's thermal conductivity k and the thermal conductance G''_{nw-sub} between the nanowire and the substrate.

If κ is assumed to be constant along the nanowire's length, the analytical solution to Eq. (5.3) is

$$T(x) = T_{sub} + \frac{A_C \cdot r}{W \cdot G''_{nw-sub}} + \left(T_m - T_{sub} - \frac{A_C \cdot r}{W \cdot G''_{nw-sub}} \right) \left[\frac{e^{\Lambda(1-x/L)} + e^{\Lambda x/L}}{1 + e^{\Lambda}} \right] \quad (5.4)$$

where A_C is the cross-sectional area, r is the volumetric Joule heating rate and T_m is the temperature of the nanowire at $x = 0$ and L where the nanowire contacts the metal leads.

The dimensionless parameter governs the shape of the nanowire's temperature profile and determines the ratio of heat dissipated to the substrate to that conducted along the nanowire's axis. As Λ increases above approximately 10, the temperature profile becomes highly flattened, while values of Λ below approximately 3 result in sharply peaked temperature profiles. Assuming that the metal contact temperature T_m is approximately equal to the substrate temperature T_{sub} , the amount of heat dissipated into the substrate is approximately equal to that leaving through the metal contacts if $\Lambda = 3.8$. If the length to width ratio is much greater than this value, heat conduction into the substrate dominates; conversely if the ratio is much smaller than the break-even value, the generated heat leaves the wire primarily through the metal contacts.

Figure 18a displays the BEL region of luminescence spectra obtained from a GaN nanowire at six dc power levels and includes best-fit simulated curves. At low temperatures only the high sides of the energy curves are used for data fitting because of the asymmetry of the curves. Consequently, only a portion of the collected data is actually used in least-squares data analysis for parameter estimation. In Fig. 18a, data that was employed for parameter estimation is shown in black while the remainder of the data is shown in gray. Minimum least-squares fits to the data indicate that the local substrate temperature T_{sub} due to laser illumination (but without Joule heating) was approximately 320 K, and that the metal contact temperature T_m may have risen as high as 460 K at the maximum applied power of 103 mW. The predicted temperature profiles of the nanowire at the different power settings are shown in Fig. 18b and reveal that the maximum temperature attained by the nanowire was approximately 900 K. Figure 18c plots the integrated

μ -PL signal as a function of input power and includes a predicted curve assuming that $E_A = 0.07$ eV. The approximate agreement between the two curves indicates that collected μ -PL spectra are consistent with the Arrhenius thermal quenching model of Eq. (5.1). A FESEM image of the nanowire before failure is shown in Fig. 18d.

Figure 18. (a) Normalized band edge μ -PL spectra (filled circles) with theoretical fits (solid lines); (b) Predicted nanowire temperature distributions based on the fits in (a); (c) Integrated μ -PL intensity as a function of input power $V \cdot I$; (d) FESEM image of nanowire and metal contacts. $L = 4.7$ mm, $W = 0.68$ mm, $T_{sub} = 320$ K, T_{σ} for $= 0.11$ meV/K, $E_A = 0.07$ eV, $k_{300K} < 70$ W/mK, $G''_{nw-sub} = 56 \pm 5$ W/mm²·K. Vertical offsets have been added to the data in (a) to enhance clarity.

From the least-squares fits, values of nanowire-substrate thermal conductance G''_{nw-sub} and the room-temperature thermal conductivity κ_{300K} can also be extracted. Based on the thermal model outlined above, the temperature profile is more sensitive to G''_{nw-sub} than κ_{300K} , and this fact is reflected in the 95% confidence intervals that can be obtained for the two variables: G''_{nw-sub} is estimated to 56 ± 5 W/mm²·K while only an upper bound of approximately 70 W/mK can be obtained for κ_{300K} . Notably, the 95% confidence intervals obtained for G''_{nw-sub} and κ_{300K} are relatively insensitive to assumed values of activation energy E_A and metal contact temperature T_m .

Figure 19. Failure current for nanowires as a function of estimated cross-sectional area with a power law fit ($R^2 = 0.90$). Data from nanowires with visibly high surface roughness (low nanowire-substrate thermal conductance G''_{nw-sub}) are not included to improve the power law fit. Inset shows SEM of one of the nanowires after failure. Pitting marks in the nanowire are indicative of GaN thermal decomposition.

As explained above, several other nanowires were characterized in a similar manner to the ones featured in Figures 17 and 18. Best-fit values of nanowire-substrate thermal conductance G''_{nw-sub} were observed to concentrate in two ranges. A high range, which includes the nanowire featured in Fig. 18, and another range, nearly an order of magnitude lower, was observed for nanowires with substantially rougher surfaces, such as the one featured in Fig. 17 (compare Figs. 17c and 18d). For nanowires with high length-to-width ratios, thermal conductivity cannot be estimated because the temperature profile of such nanowires is not sufficiently sensitive to κ but is dominated by G''_{nw-sub} . Other nanowires with low length-to-width ratios yielded upper bound estimates for k_{300K} that were similar to that of the nanowire featured in Fig. 18, which we note is substantially lower than the reported thermal conductivity of approximately 200 W/m K for GaN thin films.⁴² Since the nanowires in the present study are larger (widths W are 0.2 – 0.67 μm) than the diameter where size effects are expected to be significant (approximately 0.150 μm), additional causes for the observed low thermal conductivity compared to bulk GaN must be sought. One possibility is the significant role that point defects play in phonon scattering in single crystal GaN. The nanowires in this study have low concentrations of dislocations, which act as getters to concentrate point defects; and it is plausible that more widely distributed point defects in nanowires scatter phonons more effectively than their more tightly grouped counterparts in bulk GaN.

5.2 Failure Mechanism of GaN Nanowires

In addition to the current controlled protocol to determine thermal properties, the wires were also tested to failure. Figure 19 shows the failure current as a function of cross-sectional area for the ten wires tested with the stepped current protocol and the five additional wires mentioned earlier. A power fit of the failure current shows that the failure does not exactly correlate with current density, i.e. a sub-linear correlation with A_C is observed, which can be attributed to the fact that the substrate acts as a significant heat sink. A post-failure image of one of the nanowires is shown as an inset in Fig. 19, and displays localized breakage and pronounced pitting, especially in the region of the actual failure. Similar pitting has been identified previously as a feature of GaN thermal decomposition⁴¹ and gives strong support to the conclusion that thermal decomposition is a primary factor causing failure at high current densities.

Figure 20. TEM images showing failure of GaN nanowire due to high electric current. (a) STM probe (far right) contacts a GaN nanowire of length of 3.2 μm protruding from substrate; (b) At an applied voltage of 30 V (18 μA) precipitation of Ga balls (marked by arrows) is evident; (c) Nanowire after evaporation of Ga balls; and (d) Nanowire after failure at applied voltage of 101 V (24 μA).

At temperatures greater than approximately 1100 K, thermal decomposition of GaN samples into Ga and N_2 has been observed,⁴¹ and the rate of decomposition has been shown to increase exponentially with increasing temperature. The known thermal decomposition of GaN can be used to check the validity of the nanowire heating model presented above by estimating GaN depth loss due to thermal decomposition and comparing these values to the nanowire width. Notably, the nanowire featured in Fig. 18, as well as all other nanowires, failed at predicted temperatures a few hundred degrees below 1300 K. This is presumably because the thermal decomposition models for GaN thin films are not directly applicable to nanowires. Decomposition in nanowires is likely to be more pronounced due to higher surface area to volume ratios and the morphology of the localized failure. The agreement is good given the fact that local hot spots are fairly invisible to full field PL measurements due to the convolution of all

the temperatures along the wire combined with the roll-off of intensity with increasing temperature.

Figure 21. (a) Ga balls on the surface of a broken GaN nanowire that failed at 118 V (244 μ A). (b) HRTEM image of a Ga ball; (c, d) Electron Energy Loss Spectroscopy (EELS) images of the framed region in (a) showing that the balls are Ga. (e) Electron diffraction pattern (EDP) of a Ga ball. The high degree of radial symmetry indicates the Ga ball is amorphous.

In order to examine the failure mechanism in more detail, additional GaN nanowires grown under identical conditions were mounted in a TEM specially equipped for electrical characterization of nanomaterials. Individual GaN nanowires protruding vertically from the substrate were contacted at their free end with a STM tip as shown in Fig. 20a. Applying a voltage to the STM tip caused an electric current to flow through the nanowire and the applied voltage was increased at regular time intervals until formation of Ga balls (i.e. Ostwald ripening) became evident, which occurred at approximately 30 V (18 μ A) for the nanowire featured in Fig. 20. With increasing voltage the Ga balls evaporated (Fig. 20c), and subsequent voltage increases resulted in nanowire failure as illustrated in Fig. 20d. The separation and and evaporation of Ga and N₂ from another nanowire was confirmed by high-resolution TEM and electron diffraction, and representative images are shown in Fig. 21. Figure 21c was formed by selecting the Ga L_{2,3} energy window with a slit width of 40 eV, and Fig. 21d was formed by selecting the N K edge, also with a slit width of 40 eV. Because there is no nitrogen in the balls, they appear dark in Fig. 21d. The bar-like feature visible in the upper halves of Figures 21c and 21d is a separate, smaller nanowire and serves as a reference. It appears bright in Figures 21c and 21d because it has both

Ga and N. Importantly, there are no Ga balls on the surface of the smaller nanowire because it is unheated.

In conclusion, we have shown that it is possible to estimate the thermal conductivity and nanowire-substrate thermal conductance by comparing measured μ -PL spectra with theoretical predictions based on a one-dimensional heat transport model for Joule heated GaN nanowires. Estimates for thermal conductivity are more accurate for low-aspect ratio nanowires because heat transport along the axis of such nanowires results in axial temperature gradients that are particularly suitable for thermal conductivity estimation. Least-squares fits to μ -PL spectra obtained from such nanowires indicate that their room-temperature thermal conductivity is less than 70 W/mK, a value which is substantially lower than that of bulk GaN. Note that this value for κ is in excellent agreement with MD calculations (see Figure 16). For long nanowires, heat is dissipated primarily into the Si/SiO₂ substrate resulting in nearly flat temperature profiles that are better suited for estimating nanowire-substrate thermal conductance G''_{nw-sub} . In this work measured values of G''_{nw-sub} are observed to concentrate in two ranges: an upper range of 30-60 W/mm²/K for nanowires with relatively smooth sides and a lower range of 1.5-3.0 W/mm²/K for nanowires with relatively rough sides.

The failure mode of Joule-heated GaN nanowires was also investigated. Pitting marks concentrated near failure points indicate that nanowire failure is primarily caused by thermal decomposition. This observation was confirmed by viewing individual nanowires inside a specially designed TEM while the nanowires were heated. TEM images clearly show the formation and growth of Ga balls before nanowire failure. Comparing our results with previously validated models of GaN decomposition, we predict the critical temperature at which significant decomposition commences to be approximately 1000 K, making it possible to estimate the thermal conductivity of GaN nanowires characterized.

6. DIRECT MEASUREMENT OF GAN NANOWIRE THERMAL CONDUCTIVITY

Work is presented on thermal conductivity measurements and transmission electron microscopy of individual GaN nanowires. A thermal property measurement was performed on an ideal microfabricated structure, which omitted any thermal contact resistance between the ideal nanowire and the heater/thermometer. The results from this measurement revealed that a large mean temperature change can be observed when the nanowire was removed from the heater, thus confirming the suspended heater's ability to sense the presence of a nanostructure. The results also indicated that the thermal analysis and lumped-model estimates regarding the beam design accurately predicted the behavior of the heater/thermometer.

Measurements on single nanowires introduce an important and undesired complication: the presence of thermal contact resistance, $R_{th,c}$. In an effort to mitigate the effects of $R_{th,c}$ such that $R_{th,NW}$ could be measured more accurately, electron beam-induced deposition (EBID) Pt contacts were patterned onto the GaN nanowire. Although these Pt top contacts do not eliminate $R_{th,c}$ completely, they do significantly improve the conductance between the nanowire and the surface on which it rests. A comparison between the measured conductance data for a GaN nanowire and an estimate of the contact conductance shows that the contribution of the contact conductance is approximately two orders of magnitude larger than the total measured conductance.

This section presents experimental results regarding thermal conductivity measurements on individual GaN NWs and transmission electron microscopy on exactly the same wire. Due to the tapered nature of the GaN nanowires measured, a wire that spans from one boundary across the heater to the opposite boundary may be treated as two separate nanowires with two distinct average cross-sections. This concept can be understood from viewing Fig. 22. In this figure, the tapered GaN nanowire that spans across the heater line between boundaries can be considered as two separate nanowires, which are labeled as "1" and "2" in the illustration.

Figure 22. A single nanowire treated as two, separate wires, labeled as sections “1” and “2”. The rectangular regions on the wire represent the Pt top contacts.

6.1 The Measurement-Microscopy Cycle

A single nanowire placed on a thermal measurement platform is treated as two, separate wires in the measurement process. This task is accomplished by generating heating curves, one curve at each ambient temperature value, over the temperature range of 20 – 295 K with both sections 1 and 2 of the nanowire in tact. The heating curves generated will then provide information about the total thermal resistance of sections 1 and 2 combined, which are thermally in parallel to the side contacts that are maintained at the ambient temperature. After the thermal measurement, TEM is performed on either section 1 or 2 of the wire. Once this section has been examined, it is cut using the focused electron beam in the TEM. After this step, the measurement-microscopy process is repeated with the heating curves providing information about the thermal resistance of the remaining wire (i.e., $R_{th,1wire} = R_{th,NW2}$, if wire 1 were cut first). After the TEM process, the remaining wire is cut. With no nanowire sections remaining to provide an additional path to thermal ground, the measurement-microscopy process is repeated for a third time. For this portion of the measurement, the heating curves generated at each ambient temperature provide information about the thermal resistance of the suspended heater/thermometer, $R_{th,H1}$.

6.2 Thermal Measurements and Microscopy

Thermal conductivity measurements and TEM measurements were performed on individual GaN nanowires using the microfabricated measurement platform. Using a dual-probe nanomanipulator *in situ* of an SEM, a single GaN nanowire was placed across the suspended heater-thermometer near its midpoint. Fig. 23(a) shows the nanowire on the measurement platform. To reduce the effects of thermal contact resistance, $R_{th,c}$ EBID Pt contacts were patterned onto the nanowire using the electron beam in an SEM at locations where the nanowire made contact to the heater and the adjacent boundary. Fig. 23(b) and (c) show the GaN NW before and after the patterning of Pt contacts.⁴³

Figure 23. A microfabricated measurement platform with a nanowire placed on the suspended heater/thermometer. A micrograph taken at a relatively low magnification is given in (a), which shows the nanowire placed perpendicular to the suspended heater. Also shown are the heater's current and voltage leads, and an auxiliary thermometer. (b) A higher magnification image showing the nanowire immediately after its placement onto the heater. (c) The GaN nanowire after the patterning of EBID Pt contacts.

To perform thermal conductivity measurements on the GaN nanowires, the chip was loaded into a cryostat, placed in a vacuum state and was cooled-down to 20K. The thermal conductivity of the nanowire was measured following the aforementioned measurement-microscopy cycle and at a maximum ambient temperature of 295 K.

Cold-wire electrical resistance (R_c) data of the suspended heater/thermometer as a function of the local ambient temperature (T_c) is given in Fig. 24(a). The suspended heater exhibits a nearly

linear temperature dependence in the range of 50 – 300 K, which is a result of electron-phonon scattering in the metal heater line. At temperatures below 40 K, the phonon population in the Pt heater line decreases substantially and phonons begin to “freeze out”, with electron scattering dominated by grain boundaries and the external surface of the heater, causing resistance thermometry using metals at temperatures below ≈ 10 K to become an onerous task. Figure 24(b) shows the temperature coefficient of resistance (TCR) of the heater/thermometer, based on a numerical difference of the data in Fig. 4(a), i.e., $\alpha_0 = (R - R_0)/R_0(T - T_0)$, where α_0 is the local TCR value. For this Pt thin film structure, $\alpha_{300K} \approx 2 \times 10^{-3} \text{ K}^{-1}$, and a maximum TCR value is reached at ~ 50 K, $\alpha_{50K} \approx 5 \times 10^{-3} \text{ K}^{-1}$. For comparison to the Pt thin film, bulk Pt TCR data is given in Fig. 24(b).⁴⁴ In evaporated metallic thin films, the average grain boundary size is $\sim$ the film thickness. Numerous and small grain boundaries in thin films reduce the electron mean free path, which reduces the film’s electrical conductivity (and increases resistivity), relative to bulk values of electrical conductivity. The enhanced grain boundary scattering of electrons in thin films reduces the film’s sensitivity to temperature changes because electron-phonon scattering is no longer the single, dominant scattering mechanism, compared to bulk. This reduction in temperature sensitivity is evidenced by the data presented in Fig. 24(b). Notice that the Pt thin film exhibits a smaller resistance change for a given change in temperature, compared to bulk Pt.

Figure 24. Resistance thermometry data for the suspended heater/thermometer. (a) The cold-wire electrical resistance, R_0 , as a function of ambient temperature, T_0 . (b) The temperature coefficient of resistance (TCR), based on the values of R_0 shown in (a). For comparison, bulk Pt TCR values have been plotted as well.

With values of R_0 known as a function of temperature, the suspended Pt line is now a calibrated thermometer. To determine the thermal resistance of a GaN nanowire, heating curves were generated by sourcing a substantial electrical current such that the heater’s ambient temperature rise was ~ 10 K above ambient. This process was performed for all 3 steps of the measurement-microscopy cycle (i.e. no wires cut, one wire cut, and both wires cut) and at ambient values between 25 – 295 K at 25 K intervals. Heating-curve data taken at 295 K is given in Fig. 25(a). The data presented in this plot is a combination of three, separate and distinct measurements, which were detailed in the discussion of the measurement-microscopy cycle. Sets of data, such as those shown in Fig. 25(a), were acquired at each ambient temperature, T_0 , of interest. From Fig. 25(a), note that the heater’s mean temperature increases, for a given input power, as each

nanowire is cut. Cutting a nanowire eliminates a heat path to thermal ground.⁴⁵ The curve in which both wires are cut is a calibration curve that is a measurement of the intrinsic thermal resistance of the heater/thermometer, $R_{th,H}$. Fig. 25(b) shows a high-magnification image of one of the GaN nanowires after a measurement-cut sequence.

Figure 25. Heating curves and GaN nanowire cutting. (a) The combined heating curves generated at 295K. As each GaN nanowire is cut, a thermal path to ground is removed and for a given input power, the heater's average temperature increases. (b) TEM showing one of the GaN nanowires after the wire-cutting process. In this micrograph, the dark line at the top of the image is the suspended heater/thermometer and the dark line at the bottom of the image is the Pt contact at the lower boundary.

Once the measurement-microscopy cycle was completed, values for the thermal resistances of the 215 nm and 295 nm GaN wires were obtained as a function of temperature (see Fig. 26). As a more intuitive means of interpreting the temperature-dependent behavior of the GaN wires, the thermal conductance, which is the reciprocal of the thermal resistance, was calculated assuming negligible thermal contact resistance (this assumption is justified in the following section) and is given in Fig. 26. Observe that both nanowires exhibit a reduction in thermal conductance as the ambient temperature is reduced. This low-temperature behavior is expected due to the reduction in phonon population in the nanowire occurring at low temperatures. Also, as expected, the thermal conductance of the 295 nm wire is greater in magnitude compared to the 215 nm wire over the entire temperature range. An unexpected behavior in the data is the abrupt dip in the 295 nm wire conductance data at 225 K and the abrupt increase in the 215 nm wire conductance data between 250 and 275 K. Possible reasons for this behavior are discussed below.

Figure 26. Temperature dependent thermal conductance data for the 215 and 295 nm GaN nanowires.

Recalling that these GaN nanowires are triangularly faceted and linearly tapered, for a nanowire with widths at its ends of s_1 and s_2 , its effective cross-sectional area, A , can be formulated as $A = (3s_1s_2/4)^{0.5}$. The thermal conductivity, κ , of a GaN nanowire can be computed by relating the nanowire thermal conductance to its thermal conductivity through $\kappa = GL/A$, where L is the nanowire length. The computed values of thermal conductivity for both the 215 and 295 nm GaN nanowires are shown in Fig. 27. Also shown are values of the thermal conductivity for the 160 and 181 nm GaN nanowires measured by Guthy et al.⁴⁶ All thermal conductivity values shown in Fig. 27 are lower than bulk GaN, which is approximately 120 W/m-K at 300 K.⁴⁷ The thermal conductivity values for the 215 and 295 nm wires are very similar in value. The location where the thermal conductivity values cross is suspicious and is thought to be an artifact of the cryostat losing vacuum during this portion of the measurement, which would possibly result in the unwanted cooling of the sample holder from the colder radiation shield in this temperature range. Unfortunately, the measurement-microscopy cycle requires the destruction of the nanowire, which precludes repeating that portion of the measurement. Interestingly, the 160 and 181 nm GaN nanowires exhibit similar thermal conductivity values, with the 181 nm GaN nanowire displaying slightly lower thermal conductivity values over the entire temperature range. If the effective phonon mean free path, Λ_{ph} , was limited by the average width of the nanowire, one would expect a commensurate reduction in the thermal conductivity for a reduction in the width of the wire, i.e., $\kappa \sim d_{nw}$. However, such a dependency appears to be absent between the various wires. A slight reduction in thermal conductivity is observed between the 215 and 295 nm wires and the 160 and 181 nm wires, but these pairs of GaN wires were synthesized by different means and correlating these pairs of wires directly may not be appropriate.

Figure 27. Temperature dependent thermal conductivity data for GaN nanowires. The data for the 215 and 295 nm nanowires are results from this thesis work. The data for the 160 and 181 nm nanowires was obtained by Guthy et al. Ref. 46.

One possible explanation for the behavior of the GaN nanowire thermal conductivity is that bulk phonon scattering, rather than boundary scattering, is limiting Λ_{ph} . If a large number of defects or dislocations existed throughout the nanowire, such that $\Lambda_{ph} < \Lambda_{defect} \ll \Lambda_{boundary}$, then a reduction or increase in A would have little or no effect on the thermal conductivity for transport perpendicular to the cross-section. The possibility of phonon transport existing in a defect-limited regime for these GaN nanowires would agree with the substantial reduction in the thermal conductivity of these wires compared to the bulk value of GaN. The phonon mean free path being limited by defect scattering would also explain the observed plateau in the thermal conductivity data in the range of 200 – 300 K for the 160 nm and 181 nm GaN wires. If Umklapp scattering were present in this temperature range, the thermal conductivity data would display a decrease in value for increasing temperatures. Lastly, if the density of defects varied from wire- to-wire, then, although defect limited, a nanowire of a relatively smaller width could possess a higher thermal conductivity than a larger wire that harbors a higher defect density. The possibility of such a situation existing is plausible and would explain the slight increase in thermal conductivity of the 160 nm GaN wire compared to the larger 181 nm wire.

7. SUMMARY AND OUTLOOK

This LDRD was successful in studying the physics of defects and GaN nanowires and understanding their impact on electrical, optical and thermal properties and failure mechanism. The first development of quantitative defect spectroscopy for GaN nanowires using DLOS was achieved. This work was also the first to elucidate the spatial distribution of defects in GaN nanowires at the nanoscale using CL. Using these spectroscopy techniques, the density and energy levels of defects were determined, and their atomic origin was surmised. From these studies, it was concluded that carbon and the gallium vacancy were the dominant defects in the GaN nanowires, similar to findings for thin film GaN. Interestingly, there is strong evidence that gallium vacancies may preferentially migrate to the nanowire surface region during growth or high temperature treatment.

Robust MD methods for calculating the thermal conductivity of GaN films and nanowires was developed. When actual nanowire sizes proved too large to model directly, new analytic scaling laws were developed to calculate the dependence of thermal conductivity of the realistic physical dimensions for GaN nanowires. These advancements are at the fore of theoretical understanding of thermal conductivity in nanostructures.

Successful experimental means were devised to determine the thermal conductivity of GaN nanowires. This represents some of the earliest work on thermal properties of GaN nanowires under electrical stress. Experimental values for κ_{300K} of GaN nanowires of various widths > 200 nm showed little dependence on width, in agreement with MD calculations. However, experimental κ_{300K} values were significantly lower than calculated values for NWs using MD and scaling laws that accounted for phonon surface scattering. This suggests that phonon scattering from defects in the “core” of the nanowire is at least if not more disruptive to thermal transport than is phonon scattering at the surface.

Finally, an atomistic model describing the electrical breakdown of GaN nanowires was presented. It was suggested that excessive Joule heating due to poor thermal conductivity of the GaN nanowires leads to thermal decomposition and catastrophic failure. As the nanowire heats up, its thermal conductivity drops, causing run away heating. Gallium balls begin to form and desorb from the nanowire surface, ultimately leading to breakage and device failure. The critical current density for failure was found to depended strongly on nanowire cross-sectional area, in agreement with surface-mediated thermal transport.

Important future work in this area includes combining microscopy, spectroscopy and thermal conductivity measurements on the same GaN nanowire as a function of electrical stress. The recent advent of a platform enabling such an array of characterization methods makes such work feasible. However, there was insufficient time to capitalize on this new nanowire platform before the conclusion of this LDRD. Nonetheless, there is great potential for future work in determining the influence of nanostructure, dimensionality and defect incorporation on the thermal and opto-electronic properties of GaN nanowires.

Future MD work could extend to determining the influence of specific defects on the thermal conductivity of GaN nanowires. A good first choice would be to introduce a gallium vacancy into the supercell. With the scaling laws developed here, it can become feasible to model realistic defect concentrations of $\sim 10^{16} \text{ cm}^{-3}$ in GaN nanowires. Further, the impact of defect location, either in the nanowire core or surface, could be elucidated. Such work could give rise to new understanding of how to engineer the thermal properties of GaN nanowires.

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