CHARACTERIZATION OF SEMICONDUCTOR NANOWIRES USING RAMAN SPECTROSCOPY AND MULTIFUNCTIONAL SCANNING PROBE MICROSCOPY

By

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CHARACTERIZATION OF SEMICONDUCTOR NANOWIRES USING RAMAN SPECTROSCOPY AND MULTIFUNCTIONAL SCANNING PROBE MICROSCOPY

Abstract

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Over the past decade, research on wide bandgap semiconductor nanowires has become one of the most active areas within the nanoscience community. Particularly, there has been extensive research on ZnO and GaN nanowires due to their promising applications in next-generation optoelectronics and highly efficient photovoltaics. Central to realizing these applications is a fundamental understanding of physical properties, such as impurity incorporations, phonon dynamics, and carrier transport. Multi-functional scanning probe microscopy and spatially resolved Raman spectroscopy are suitable tools for studying these properties in individual nanowires.

Specifically, Raman spectroscopy, aided by mass spectrometry, was used to identify unintentional impurities in ZnO and GaN nanowires and their incorporation route. Phonon dynamics, in particular the enharmonic phonon coupling strength, was also studied by Raman spectroscopy. A near-field scanning photocurrent microscopy was used to directly measure minority carrier diffusion length and to determine its diameter dependence in individual ZnO nanowires. The origin of this diameter dependence was elucidated by surface photovoltage...
measurements using scanning Kelvin probe force microscopy and finite-element simulations. In addition, a demonstration of probing heat transport along nanowires and across various nanowire device interfaces using scanning thermal microscopy combined with Raman spectroscopy was also presented.
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This dissertation is dedicated to my wonderful, loving and caring husband Shoresh.
Chapter 1 Wide Band-gap Semiconductors

Semiconductor nanowires\(^1\)\(^-\)\(^3\) have recently emerged as building blocks of many electronic, photonic and energy conversion applications. In this chapter I will summarize the general properties and practical applications of wide-band-gap semiconductors that are the subject of this research.

1.1 Gallium Nitride

Gallium Nitride (GaN) has attracted significant research attention amongst group III-nitride semiconductors due its wide band-gap (3.4 eV), which makes it suitable for variety of electronic and optoelectronics applications. In particular, GaN has been successfully used in visible and UV optoelectronics such as high brightness light emitting diodes\(^4\) (LED) and laser diodes\(^5\). It has also been used in field effect transistors\(^6\) due to their good electron transport properties. On the other hand, GaN has a high thermal conductivity and stability and large dielectric breakdown field which make it a potential candidate in high temperature/power and high-speed electronics.

The other advantage of this group III-nitride is the capability of its direct band gap to be tuned by doping and composition modulation to cover the whole solar spectrum\(^7\), making GaN a perfect material for photovoltaic applications. GaN thin films have shown high density of defects due to their lattice mismatch to the growth substrate which deteriorates its device performance. In contrast, GaN nanowires have shown to be dislocation free single crystals.

GaN nanowires have been grown using a variety of techniques including metalorganic chemical vapor deposition\(^8\),\(^9\), laser ablation\(^10\), arc discharge\(^11\) and chemical vapor deposition (CVD)\(^12\)-\(^14\). We have chosen to use the CVD process due to its low cost and simplicity of the procedure but
more importantly the ability to control over several aspects of growth such as diameter and length of the nanowires.

The synthesis of GaN nanowires is described in detail later in Chapter 3. In short, a thermal chemical vapor deposition system (EasyTube 2000, First Nano) was used for the growth. Gallium pellets (Alfa Aesar, 99.9999%), and anhydrous NH₃ (99.99%) were used as the gallium and the nitrogen sources, respectively, with the growth temperature of 920 °C and the pressure of 500 Torr. A mixture of Ar and H₂ was used as the carrier gas. These nanowires were grown on c-plane sapphire substrates coated with nickel nitrate hexahydrate (Alfa Aesar, 99.9985%) diluted in ethanol.

1.2 Zinc oxide

Due to its wide band gap, large exciton binding energy¹⁵ and high energy radiation stability, zinc oxide¹⁶ (ZnO) is becoming a promising alternative to GaN in optoelectronic applications. It is one of the most well studied functional oxide semiconductors particularly as a bulk material. ZnO band gap is ~ 3.3 eV at 300K, similar to the GaN band gap, but the advantage of ZnO over GaN is its large exciton binding energy (60meV) and the availability of high quality bulk single crystals. It makes this cheap environmentally friendly material, a very good candidate for lasing with low UV lasing threshold and high emitting efficiency. ZnO can also be used as GaN growth substrate for their small lattice mismatch.

Because of its piezoelectric properties, ZnO has been focus of many research groups for applications as ultrasonic transducers and nanogenerators. It has also been predicted to have above room temperature Curie temperature and therefore it is investigated as a spintronic material.
There has been extensive research on ZnO mainly due to its excellent electrical and optical properties. ZnO is a transparent conducting oxide which has been used in variety of electronic and optoelectronic applications. In particular, ZnO nanowires have emerged as potential building block in high speed and low power devices including transparent and flexible electronics\textsuperscript{17}, high gain UV photodetector\textsuperscript{18}, field effect transistors\textsuperscript{19}, nanosensors and nanolasers\textsuperscript{20}.

Excitonic solar cells\textsuperscript{21} are the other venue for semiconductor nanowires because of their long absorption path length, fast carrier transport and charge separation. In particular, ZnO nanowires have been explored as photoanodes in dye sensitized solar cells\textsuperscript{22-24} due to its wide band gap and high electron mobility.

Despite all the applications, major disadvantage of ZnO is the lack of reliable and reproducible p-type material. Recently, there have been several reports on successful p-type doping of ZnO specifically in nanostructures\textsuperscript{25} which opens up opportunities for broad electronics and photonics applications.

ZnO nanomaterials have been synthesized using different methods including thermal evaporation, MOCVD\textsuperscript{26}, laser ablation, sol gel\textsuperscript{27}, and chemical vapor deposition\textsuperscript{28,29}. CVD is the most widely used technique in semiconductor oxide growth which gives us the ability to control the nanowire diameter, length, orientation, composition and location.

The synthesis of ZnO nanowires was carried out in a commercial CVD system. Gold catalyst was used to catalyze the nanowire growth on silicon substrates. A mixture of ZnO (Alfa Aesar, 99.999\%) and graphite (Alfa Aesar, 99.9995\%) powders in a quartz boat was used as the Zn source following the reaction, \(\text{ZnO}(s) + \text{C}(s) \rightarrow \text{Zn}(\nu) + \text{CO}(\nu)\). This quartz boat was heated to 950\(^\circ\)C by a local heater, and the generated Zn vapor was carried by a flow of Ar to the growth
zone, where O\textsubscript{2} was injected to enable the nanowire growth. The temperature of the growth zone was held at 820°C during the growth at a pressure of 7.5torr. More details on the growth procedure are provided in chapter 3.

1.3 Outline of the dissertation

Chapter 2 describes experimental techniques employed in this work. The rest of the dissertation includes five first author papers which were the result of my research. I was the main contributor in all of them. In chapter 3,\textsuperscript{30} we report the observation of unintentionally incorporated nitrogen-related complexes in ZnO and GaN nanowires grown by the catalytic vapor-phase transport method. In particular, our experimental findings from Raman scattering spectroscopy and mass-selected time-of-flight particle emission measurements suggest the presence of interstitial nitrogen molecules that are formed during the nanowire growth.

We have determined quantitatively the third-order anharmonic phonon coupling matrix elements in ZnO nanowires, via detailed calculations of phonon self-energy and analysis of the asymmetric E\textsubscript{2}\textsuperscript{high} phonon peak at room temperature in Chapter 4.\textsuperscript{31} Chapter 5 (ref.32) and Chapter 6 (ref. 33) are focused on measurement of the minority carrier diffusion length, L\textsubscript{D}. It was first directly measured in individual ZnO nanowires by a near-field scanning photocurrent microscopy technique. The diameter dependence of L\textsubscript{D} suggests a diameter-dependent surface electronic structure, manifested by an increase in the density of mid-bandgap surface states with the decreasing diameter, as the main origin of surface effects on minority carrier transport.

Next, based on single-nanowire surface photovoltage measurements and finite-element electrostatic simulations, we determine the surface state density, N\textsubscript{s}, in individual n-type ZnO nanowires as a function of nanowire diameter. In general, N\textsubscript{s} increases as the diameter decreases. This identifies an important origin of the diameter dependence of the surface recombination
velocity mentioned earlier in chapter 5, which has been commonly considered to be independent of the diameter. Furthermore, through the determination of the surface carrier lifetime, we suggest that the diameter dependence of the surface state density accounts for the rather abrupt transition from bulk-limited to surface-limited carrier transport over a narrow nanowire diameter regime (30 – 40 nm). These findings are supported by the comparison between bulk-limited and surface-dependent minority carrier diffusion lengths measured at various diameters.

In Chapter 7, using an approach combining scanning thermal microscopy (SThM) and spatially revolved Raman spectroscopy, we have investigated quantitatively the heat dissipation characteristics in substrate-supported and suspended (with asymmetric type of contacts) current-carrying GaN nanowires with diameters of ~40–60 nm, where the phonon confinement is expected to play an important role in thermal transport. Besides providing quantitative insight into heat dissipation characteristics, our results also reveal aspects, particularly the topography-related thermal signals and the relative significance of various tip–sample thermal transfer processes, that are important to advancing the applications of SThM technique in nanoscale thermal characterizations.
Chapter 2 Experimental Techniques

In this chapter, I discuss the experimental techniques I mainly used throughout my research.

2.1 Chemical Vapor deposition

Chemical Vapor Deposition (CVD) technique is based on vapor liquid solid (VLS) growth mechanism first proposed by Wagner and Ellis in 1960s. It has been proven to be the most general and convenient method for synthesis of various types of one-dimensional nanowires catalyzed by metal particles or thin films. Using CVD, nanowire growth with controlled diameter, length, precise growth orientation and architecture modulation in large quantities can be realized.

In the VLS process, the sources are thermally evaporated and the vapor molecules are transferred to the substrate at lower temperature in the middle of tube furnace via an inert carrier gas. Then the vapor molecules as well as the reaction gas diffuse into the catalyst nanoclusters. The liquid catalytic alloy supersaturates with vapors and acts as a preferred nucleation site for oriented solid growth. The growth continues as long as the catalyst remains liquid at the eutectic temperature. The existence of the catalyst at the end of the nanowires is the evidence of VLS growth.

Despite the successful synthesis of different composition nanowires, the drawback of the CVD technique is the inevitable contamination of the nanowires with the metal catalyst as well as other impurities introduced into the furnace in low vacuum.
2.2 Raman Spectroscopy

Raman spectroscopy is a nondestructive optical characterization technique for studying different aspects of materials including lattice, electrical and thermal properties\textsuperscript{38-40}. Light scatters both elastically and inelastically when irradiated on the materials. Raman scattering is the inelastic scattering of electromagnetic wave from molecular vibrations in materials. The intensity of Raman scattered light is a few orders of magnitude smaller than the elastic scattering (Rayleigh) but it can be observed using high intensity coherent exciting source such as lasers. In classical theory, the electric field of the electromagnetic wave with frequency $f$ changes the dipole moment ($P$) of the molecules. When molecules are vibrating with frequency $f_i$, the nuclear displacement $q$, given by $q = q_0 \cos(2\pi f_i t)$, interacts with the electric field and gives rise to the Raman shift as follows,

$$E = E_0 \cos(2\pi ft);$$

$$P = \alpha E;$$

where $\alpha$ is the polarizibility of the material, $\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 q$, and $\alpha_0$ is the polarizability at the equilibrium position.

$$P = \alpha_0 E_0 \cos(2\pi ft) + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos(2\pi ft) \cos(2\pi f_i t) = \alpha_0 E_0 \cos(2\pi ft) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \{ \cos[2\pi(f + f_i)t] + \cos[2\pi(f - f_i)t]\}. \quad (2.3)$$

The first term in equation 2.3 describes the dipole moment that radiates the Rayleigh scattering; the second moment is responsible for the anti-Stokes Raman and the last one for the Stokes Raman scattering.
In a crystalline material, the atoms and molecules are vibrating in a lattice structure and according to quantum mechanics lattice vibrations are described by phonons in analogy with the photons of the electromagnetic waves. To observe Raman spectra of a crystal, both momentum and energy should be conserved while the photon interacts with the lattice phonons. Since lattice vibrations are observed in the low frequency region ($\lambda \sim 10^{-2}$-$10^{-4}$ cm$^{-1}$) this only takes place at the center of the Brillouin zone where the momentum is almost zero. Taking into account the lattice symmetries and group theory lead to the selection rules for Raman spectroscopy which further results in crystal characterization. A quantum mechanical simplistic explanation of the Raman scattering is that the photon with frequency $f$ excites the electrons in the crystal from ground state to a virtual state and the electron relaxes into the ground state by emitting a photon with a slightly different frequency, $(f \pm f_i)$, where $f_i$ is the frequency of the annihilated or created lattice phonon. In chapters 3, 4 and 7 we take advantage of this technique to study the properties of ZnO and GaN nanowires.

2.3 Scanning Probe Microscopy (SPM)

Scanning probe microscopy$^{41-44}$ is a multifunctional high resolution technique based on the conventional atomic force microscope and capable of measuring various physical properties of nanomaterials. The invention of scanning tunneling microscope$^{45}$ and later atomic force microscope$^{46}$ has led to the development of variety of scanning probe techniques. The idea behind the microscopes is to keep a very sharp tip close to the sample using a feedback loop and analyze the surface. Various interactions between sample and the probe including mechanical, electrical, chemical and magnetic can be explored at nanometer scale. The technique can operate in ambient air, under vacuum or in the liquid environment to analyze insulator, semiconductor, metallic or biological materials.
Using multifunctional SPM, my primary PhD research aims to establish a fundamental knowledge of carrier transport properties of semiconductor nanowires. Here are the basic principles of the techniques that I used in this work.

2.3.1 Scanning Photocurrent Microscopy

The resolution of the conventional optical microscopy is limited by the diffraction limit, \( \lambda/(2NA) \), where \( \lambda \) is the wavelength of the incident light and NA is the numerical aperture. In the near-field scanning optical microscope (NSOM), the sample is illuminated through an aperture with the size smaller than the light wavelength, kept tens of nanometers away from the sample surface which leads to an image resolution of the order of aperture size. The aperture is generally a tapered fiber probe which is coated with metal to confine the light inside the fiber.

Scanning Photocurrent Microscopy (SPCM) is a SPM technique implemented on NSOM that can provide insight into local carrier transport properties such as carrier diffusion length. SPCM uses the focused laser spot from the fiber probe to locally generate excess carriers in the material resulting in a photocurrent. From the spatial variation of this photocurrent, which is very sensitive to electric field, carrier transport properties can be extracted. Details of the experiment are discussed later in chapter 5.

2.3.2 Scanning Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM) is a powerful technique to study electrostatic potential of surfaces on a nanometer scale. This method has been widely used to characterize the electronic structure of surfaces, semiconductor devices and most recently organic materials. When two different materials are brought into contact, there will be a contact potential difference (CPD) at the interface due to the difference between their work functions (\( \varphi_1 \) and \( \varphi_2 \)), \( CPD = \varphi_1 - \varphi_2 \).
\( \frac{1}{e} (\varphi_2 - \varphi_1) \). KPFM images the CPD on the surface. Specifically, an AC voltage with a DC offset is applied to a conducting AFM tip\textsuperscript{59-61},

\[
V = V_{AC} \sin \omega t + V_{DC}. \tag{2.4}
\]

The electrostatic force between the probe and the sample in the z direction is

\[
F = \frac{1}{2} \frac{dC}{dz} V^2 = \frac{1}{2} \frac{dC}{dz} (CPD - V_{AC} \sin \omega t - V_{DC})^2, \tag{2.5}
\]

where \( C \) is the capacitance of the system. The squared voltage results in three different components,

\[
F = F_{DC} + F_\omega \sin \omega t + F_{2\omega} \cos 2\omega t \tag{2.6}
\]

\[
F_{DC} = \frac{1}{2} \frac{dC}{dz} (CPD - V_{DC})^2 + \frac{V_{AC}^2}{2} \tag{2.7}
\]

\[
F_\omega = - \frac{dC}{dz} (CPD - V_{DC})V_{AC} \tag{2.8}
\]

\[
F_{2\omega} = - \frac{1}{2} \frac{dC}{dz} V_{AC}^2 \tag{2.9}
\]

By varying the tip DC offset and nullifying the \( \omega \)-component of the electrostatic force, KPFM measures the surface voltage, CPD.

In chapter 6, we use KPFM technique to measure surface photovoltage (SPV) and subsequently the diffusion length of the ZnO nanowires. Particularly, an above-bandgap laser emission was used to globally illuminate a single nanowire Schottky diode. The photo generated minority carriers (holes in this case) change the surface band bending leading to a change in CPD between the tip and the nanowire. The CPD was recorded simultaneously with the topography as a
function of the probe position both under the illumination and in the dark. The surface photovoltage, defined as the difference between the \( \text{CPD}_{\text{illuminated}} \) and the \( \text{CPD}_{\text{dark}} \), is a function of the excess carrier concentration \( \Delta P(x) \). The minority carriers created close to the Schottky diode diffuse into the junction, therefore the carrier concentration increase away from the electrode edge. The hole diffusion length (\( L_i \)) is then obtained from the SPV dependence to the hole concentration at the surface\(^{62}\).

\[
SPV = C \ln\left\{1 + \frac{\exp\left[-x/L_i\right] + g\tau}{(\Delta P_0)}\right\}
\]

(2.10)

Where \( g \) is the generation rate and \( \tau \) is the effective hole bulk recombination lifetime. If the number of holes generated by the global optical illumination is large enough to saturate the surface states, which, as a result, can no longer trap holes, then this \( L_i \) represents the intrinsic, i.e. bulk limited carrier diffusion length.

### 2.3.3 Scanning Thermal Microscopy

Similar to other SPM techniques, scanning thermal microscopy\(^{63}\) (SThM) is also based on the very sharp tip in close proximity of the sample, which gives high resolution images of thermal profile, electrical resistance, Joule expansion and more depending on the probe used in the measurement. The thermal probe is the key element of SThM\(^{64}\). The spatial resolution greatly depends on tip-sample heat transfer mechanism. There are two approaches in SThM\(^{65}\), namely, active and passive. In the passive mode a thermocouple probe is used and maps the temperature of the heated sample, whereas in the active mode the probe is also heated and transfer heat to the sample and as a result it can measure local thermal properties of the material. Thermocouple probe basically is a gold and platinum junction thermometer at the tip of the probe.
In chapter seven we used thermoresitive probe to measure the electrical resistivity of the device. The probe consist of two Pt wires running through a glass fiber, a small amount of current (0.05 mA) is going through the Pt wire junction, the change in the electrical resistance of this junction, obtained by measuring the voltage change across a Wheatstone bridge, corresponds to the temperature variations at the wire junction.
Chapter 3 Unintentionally Incorporated Nitrogen-Related Complexes in ZnO and GaN Nanowires

Semiconductor nanowires have been intensively explored as building blocks for the next-generation electronic and opto-electronic devices\(^1\). Significant progress\(^5, 18, 24, 66-72\) has been made recently in demonstrating potentially superior and/or unique characteristics of devices based on these nanomaterials. Further advances towards real-world applications require a reliable and precise control of material properties, which, to a large extent, are determined by impurities present in the material. To this end, controlled incorporation of functional impurities enables an impurity-engineering approach, whereby novel material properties can be engineered based on the interactions between impurities and the one-dimensional material host. On the other hand, unintentional impurity incorporation, such as the diffusion of Au catalyst atoms into nanowires during the growth,\(^49\) can be significant in determining nanowire electronic properties. Therefore, efforts towards identifying impurity species, especially those incorporated unintentionally, as well as understanding their microscopic structures and effects on material properties, are critical to advancing nanowire-based device technologies.

In this chapter, using Raman scattering spectroscopy and mass-selected time-of-flight particle emission techniques, we show the presence of *unintentionally* incorporated nitrogen-related complexes (most likely interstitial nitrogen molecules) in ZnO and GaN nanowires grown by the catalytic vapor-phase transport method. As nitrogen-related complexes/molecules (which are donors in ZnO\(^73, 74\)) strongly compensate the p-type doping with nitrogen in ZnO\(^74, 75\) and introduce localized mid-bandgap energy states in GaN,\(^76, 77\) these results have significant implications for current efforts on realizing high-performance opto-electronic device applications based on these nanomaterials. In addition, with the catalytic vapor-phase transport method as one
of the most widely used approaches for nanowire synthesis, the experimental findings presented here might be relevant for many nanowire systems, signifying the necessity of more studies on unintentional impurity incorporation in these nanomaterials.

The synthesis of ZnO and GaN nanowires was carried out in a commercial 3-zone quartz-tube-furnace chemical vapor deposition system (ET 2000, First Nano). Various metal catalysts (Au, Ag, and Ni) were used to catalyze the nanowire growth on various substrates (Al₂O₃, Si, and Si/SiO₂). For ZnO nanowire synthesis, a mixture of ZnO (Alfa Aesar, 99.999%) and graphite (Alfa Aesar, 99.9995%) powders in a quartz boat was used as the Zn source. This quartz boat was heated to 950°C by a local heater, and the generated Zn vapor was carried by a flow of Ar to the growth zone, where O₂ was injected to enable the nanowire growth. The temperature of the growth zone was held at 820°C during the growth at a pressure of 7.5torr. For GaN nanowire synthesis, gallium pellets (Alfa Aesar, 99.9999%) and anhydrous NH₃ (99.99%) were used as the gallium and the nitrogen sources, respectively, with the growth temperature of 920°C and the pressure of 500 torr. In both cases, the quartz reactor was pumped to the base pressure (≤1 mtorr) by a mechanical dry pump and then purged with Ar before the growth. After the growth (the duration of which is 30 minutes), the reactor was first pumped to the base pressure and then was cooled down under a flow of Ar. Separate sets of quartzware were used for ZnO and GaN nanowire growths to prevent cross contaminations.
Raman measurements in the backscattering configuration were carried out using a Renishaw InVia Raman microscope, with the excitation provided by a 442nm emission from a dual-line Kimmon He-Cd laser. Mass-selected time-of-flight (TOF) neutral particle emission measurements were performed during pulsed excimer laser irradiation. These experiments were performed in vacuum (base pressure $7 \times 10^{-8}$ Pa) with a Lambda Physik Lextra 200 laser operated at 193nm (ArF excimer, 15ns pulses) focused to a 0.01 cm$^2$ spot. Emitted neutral atoms/molecules were mass selected with a UTI 100C quadrupole mass spectrometer (QMS) and detected in a time-resolved fashion (time of flight). The schematic experimental setup is shown in Figure 3.3 (a). The output of the ion detector (a channeltron electron multiplier) was pulse-counted with an EG&G PARC 914P multichannel scalar, averaged over 200 laser pulses.

Figure 3.1 (a) shows a typical scanning electron microscopy (SEM) image of as-grown ZnO nanowires on a Si/SiO$_2$ substrate (with the SiO$_2$ thickness of ~500 nm) with 50 nm Au colloids as the catalysts. A
high-magnification SEM image (inset) shows a residual catalyst on the tip of a nanowire, consistent with the catalyzed growth process. Growths using 20 nm, 50 nm, and 80 nm Au colloids yielded nanowires with the average diameters of 23 nm, 59 nm, and 87 nm, respectively. Similar growth characteristics have been observed for GaN nanowires (not shown here). The low-frequency (240-650 cm\(^{-1}\)) Raman scattering spectrum of ZnO nanowires [Figure 3.1 (b)] exhibits typical features of the wurtzite-type ZnO lattice,\(^78\) with the \(E_2^{\text{high}}\) phonon and the \(E_1\) longitudinal optical (LO) phonon modes at 439 cm\(^{-1}\) and 585 cm\(^{-1}\), respectively. Additional peaks are observed at 332 cm\(^{-1}\) and 382 cm\(^{-1}\), which can be contributed to a difference mode (\(E_2^{\text{high}} - E_2^{\text{low}}\)) and the \(A_1\) transverse optical (TO) phonon, respectively.\(^78\) We have attempted to obtain Raman spectra from single ZnO nanowires; however, no Raman signal can be detected. This is probably due to the scattering geometry of our experimental setup and the ZnO nanowire growth orientation.\(^79\) In contrast, in the case of Au-catalyzed GaN nanowires, single nanowire Raman spectrum was obtained [Figure 3.1 (c)]. Besides the \(A_1\) LO phonon peak (~ 721 cm\(^{-1}\)), an Figure 3.2: Raman spectra of (a) as-grown ZnO and GaN nanowires (NWs) with the inset showing the Raman spectrum of a blank Si substrate and (b) the same single GaN nanowire before (as-grown) and after an annealing in NH\(_3\).
additional peak can be seen at ~ 254 cm$^{-1}$. This peak has been observed in wurtzite GaN nanowires$^{80-82}$ and attributed to the zone-boundary phonons activated by the lattice disorder,$^{80}$ the presence of which is consistent with the large width (~27 cm$^{-1}$ obtained by the Lorentzian fits) of the A$_1$ LO phonon peak observed here.

While the low-frequency Raman spectra of ZnO and GaN nanowires exhibit distinct features corresponding to their different crystal lattices, their high-frequency Raman spectra, shown in Figure 3.2 (a), have very similar characteristics in addition to the vibrational mode of molecular nitrogen in the ambient air observed at 2330 cm$^{-1}$. Specifically, a peak at 2306 cm$^{-1}$ can be observed for both ZnO and GaN nanowires,$^{84}$ indicating a common origin of this vibrational mode. This peak is not related to the substrates, where only the 2330 cm$^{-1}$ peak was observed [inset to Figure 3.2 (a)]. This vibrational mode has been observed in nitrogen-doped bulk ZnO and attributed to nitrogen-related complexes.$^{85,86}$ The observation of this mode here indicates the presence of such impurity complexes in both as-grown ZnO and GaN nanowires. We note that Au-H molecules (with a vibrational frequency of ~ 2305 cm$^{-1}$),$^{87}$ possibly formed during the Au-catalyzed nanowire growth,$^{49}$ can also account for the observed Raman peak. However, this 2306 cm$^{-1}$ peak is also present in the Raman spectra of nanowires grown with Ag and Ni catalysts as well as those grown on Al$_2$O$_3$ substrates (not shown here), excluding the potential contributions from catalysts and substrates. In addition, this vibrational mode does not correspond to any known carbon or hydrogen-related complexes,$^{88-91}$ which are often present in ZnO.

To verify the nitrogen-related origin of this vibrational mode, we have carried out post-growth NH$_3$ annealing procedures with the purpose to introduce more nitrogen atoms into nanowires. While ZnO nanowires seem to dissociate during the NH$_3$ annealing, as the case for bulk ZnO,$^{92}$
no morphology change was observed for GaN nanowires after the annealing. Figure 3.2 (b) shows the Raman spectra of the same single GaN nanowire before and after the annealing in NH$_3$ at 600°C for 30 minutes, and a significant increase in the 2306 cm$^{-1}$ peak intensity can be observed. We have investigated a number of single GaN nanowires, and the increase in the peak intensity after the NH$_3$ annealing was observed in most cases. This clearly points to nitrogen-related complexes as the origin of the vibrational mode observed at 2306 cm$^{-1}$.

While nitrogen-related complexes, in particular interstitial nitrogen molecules, can readily form in GaN, the presence of such impurity complexes is unexpected for intrinsic ZnO nanowires. To gain further insight into the nature of these impurity complexes, we have carried out laser induced desorption studies. In particular, we employ the mass-selected time-of-flight (TOF) particle emission technique on ZnO nanowires as presented below. We expect that nitrogen-containing emissions would confirm and reflect the locus of nitrogen-related complexes in nanowires.

These experiments were performed on ZnO nanowires grown on a sapphire substrate (transparent to the laser). Significant emissions at 28 amu/e (solid black line) were observed, as shown in Figure 3.3 (b). The TOF is defined as the time interval between the laser pulse and the arrival of the ions at the detector. To confirm that the observed signal at 28 amu/e is due to diatomic nitrogen molecules and not carbon monoxide molecules (which have the same mass as the nitrogen molecules), measurements at 28 amu/e were correlated with those at 14 amu/e (nitrogen) and 12 amu/e (carbon). Diatomic molecules with the same masses can often be unambiguously identified by the presence of atomic fragments produced by the electron impact in the quadruple ionizer (“cracking” of the molecules), as the TOF of the atomic fragments is similar to that of their parent molecules (the small differences occur in the TOF from the ionizer
to the detector, typically only a few µs). If the signal at 28 amu/e is due to carbon monoxide molecules, we would expect the signal at 28 amu/e to be accompanied by a very similar TOF signal at 12 amu/e (carbon). Conversely, if the signal at 28 amu/e is due to nitrogen molecules, we expect the signal at 28 amu/e to be accompanied by a signal at 14 amu/e (nitrogen) with a very similar TOF. As shown in Figure 3.3 (b), signals at 12 and 14 amu/e were both detected. Importantly, the temporal behaviors of the signals at 28 amu/e and 14 amu/e are quite similar, and both differ markedly with the temporal behavior of the significantly faster TOF observed at 12 amu/e. Thus we can confidently conclude that the signal at 28 amu/e is due to diatomic nitrogen molecules and not carbon monoxide molecules based on the results shown in Figure 3.3 (b); likewise, we can conclude that the observed carbon emission is not related to carbon monoxide molecules. Similar analysis on methane (CH₄) cracking fractions shows that CH₄ is also not the source of mass 12 (carbon). We conclude that carbon comes directly from ZnO nanowires as an atomic emission. We note that carbon is a common unintentional dopant in ZnO, and the graphite powers used for ZnO nanowire growth might be a potential source of carbon. Further, to determine whether the nitrogen molecules in ZnO nanowires reside on the surface or in the bulk, we have examined the behaviors of molecular nitrogen emission with the laser fluence. Species residing on the surface are typically desorbed at lower fluences, starting with the first few pulses incident on the surface, and are quickly depleted. On the other hand, emissions of species residing in the bulk are characterized by threshold-like behaviors as a function of the laser fluence. We have observed a clear threshold for the molecular nitrogen emission of ~ 80 mJ/cm². Additionally, we have monitored oxygen and zinc emissions at 16 amu/e and 64 amu/e simultaneously (not shown here), and the molecular nitrogen signal was found to follow the presence and disappearance of these ZnO-derived signals.
Figure 3.3: (a) Schematic experimental setup of the mass-selected time-of-flight particle emission measurements; (b) Signals at 12 amu/e (solid red line indicated by the arrow), 14 amu/e (dashed blue line), and 28 amu/e (solid black line); (c) signal at 28 amu/e (solid black line) fitted to a Maxwell-Boltzmann velocity distribution (dashed red line) with an effective temperature of 1090K. A 193-nm irradiation at a fluence of 240 mJ/cm² was used.
These observations are consistent with the presence of nitrogen molecules inside ZnO nanowires. Furthermore, the molecular nitrogen TOF signal is well described by a Maxwell-Boltzmann velocity distribution\(^9\) shown in Figure 3.3 (c). This indicates that the emission rate of nitrogen molecules is limited by a thermal effusion process during each laser pulse. From the fittings, the effective temperature of nitrogen molecules was determined to range from 580 K at 120 mJ/cm\(^2\) to 1210 K at 300 mJ/cm\(^2\). The latter temperature is near the onset of optical breakdown and rapid vaporization of single crystal bulk ZnO in ultra-high vacuum. This thermal effusion process further confirms the location of nitrogen molecules inside the crystal lattices of ZnO nanowires.

These results lead us to propose that interstitial nitrogen molecules are the origin of the observed vibrational mode at 2306 cm\(^{-1}\) in ZnO and GaN nanowires. This is consistent with previous experimental findings\(^9\) that the vibrations of interstitial nitrogen molecules in various materials, including ZnO and GaN, have the same energy level splitting due to their minimal but finite interactions with crystal lattices. We also have carried out infrared absorption experiments, and this vibration mode was not observed. This is expected as nitrogen molecules are Raman active but infra-red inactive. While further studies are needed to validate the proposed origin of the observed vibrational mode, the presence of nitrogen-related complexes/molecules is clearly supported by Raman spectroscopy and particle emission results presented above. Next we discuss the possible routes of nitrogen incorporation into nanowires. In the case of ZnO nanowires, given the base pressure of \(\leq 1\) mtorr in the reaction chamber, the residual background nitrogen gas is a possible source of nitrogen molecules.
We note that nitrogen molecules dissolve easily in molten metals and become atomic nitrogen.\textsuperscript{100} This process is expected to become more efficient with the large surface area of metal nanocatalysts. These dissolved nitrogen atoms then diffuse into nanowires during the growth. An interesting issue arises as to whether these nitrogen atoms occupy oxygen sites as p-type dopants in ZnO. Previous studies\textsuperscript{101} have shown that, in bulk nitrogen-doped ZnO, after annealing at a temperature of 800°C for 3 minutes, nitrogen atoms initially occupying oxygen sites as the p-type dopants move to interstitial locations and form molecules, compensating the p-type doping. Here, with the ZnO nanowire growth temperature of 820°C, the incorporated nitrogen atoms are likely to form interstitial nitrogen molecules, consistent with our observations. Indeed, these ZnO nanowires appear to be n-type semiconductors based on our electrical measurements (not shown here). A similar nitrogen incorporation route is also expected for GaN nanowires. In this case, while nitrogen atoms can also diffuse into nanowires via the side walls from the growth ambient (NH\textsubscript{3}), as evidenced by the post-growth annealing results presented above, the dissolution of NH\textsubscript{3} in metal nanocatalysts\textsuperscript{100} followed by the diffusion of nitrogen atoms into nanowires is likely to be the dominant route. This is supported by the Raman spectra obtained at various locations on a single GaN nanowire (Figure 3.4).

While most single as-grown GaN nanowires we have investigated exhibit rather weak Raman
signals at 2306cm$^{-1}$, some have relatively strong signals so that a reliable comparison of the peak intensities is possible. As shown in Figure 3.4, the vibrational mode due to nitrogen-related complexes/molecules show little variance along the nanowire, indicating that nitrogen incorporation via the catalysts, rather than the diffusion through the side walls, is the dominant process.

We note that, among a wide array of methods available for nanowire synthesis, the catalytic vapor-phase transport technique is one of the most widely used approaches. This suggests that, while the variations in the growth parameters may have an impact on the incorporation of nitrogen atoms and the formation of related complexes, the results presented here are broadly relevant. In particular, residual nitrogen molecules may be present in most low-pressure and atmospheric nanowire growth reactors. Additionally, the incorporation of nitrogen atoms via metal nanocatalysts, as a result of the efficient dissolution of nitrogen molecules in molten metals, might be a universal phenomenon during the metal-catalyzed nanowire growth. For ZnO nanowires, the formation of nitrogen-related complexes/molecules introduces unintentional n-type dopants$^{73, 74}$ and is also a major compensation mechanism for the p-type doping using nitrogen.$^{73-75, 102}$ Low-temperature (<800$^\circ$C) growth might be desirable in suppressing this type of compensation, as suggested for bulk ZnO.$^{74}$ In GaN nanowires, nitrogen-related complexes/molecules introduce localized energy levels in the band gap$^{76, 77}$ and thus play an important role in determining optical and carrier transport properties. In addition, the unintentional incorporation of nitrogen atoms and related complexes in other nanowire systems, including GaP,$^{103}$ Si,$^{104}$ and Ge,$^{105}$ can also have profound effects on their electronic and opto-electronic properties. This calls for more studies on unintentional impurity incorporations and their effects on nanowire material properties.
Chapter 4 Anharmonic Phonon Coupling in ZnO Nanowires

Recently, semiconductor nanowires have been attracting much research interest due to their novel physical properties. Among these nanomaterials, ZnO nanowires have been demonstrated to exhibit enhanced mechanical strength\textsuperscript{106} and Young’s modulus,\textsuperscript{107} novel structural phase transformations,\textsuperscript{108} as well as to enable highly efficient mechanical-to-electric energy conversions.\textsuperscript{70} The anharmonicity of lattices contributes significantly to the underlying mechanisms of these unique properties.

In crystalline materials, the description of lattice vibrations and potentials is a critical issue in developing a fundamental understanding of charge carrier dynamics, thermal expansion and transport, mechanical deformations, and phase transformations. Particularly, anharmonic (cubic, quartic, or higher-order) terms in the expansion of the lattice potential energy are of great importance. A manifestation of effects arising from these anharmonic terms is phonon-phonon interactions, the characteristics of which can thus provide insight into the anharmonicity of lattice vibrations. To this end, Raman spectroscopy is a powerful tool that enables direct access to phonon interactions.

In this work, we have used Raman spectroscopy to investigate the anharmonic phonon coupling in ZnO nanowires. We have specifically focused on the $E_2^{\text{high}}$ phonon mode that decays anharmonically via three-phonon processes.$^{78, 109}$ By analyzing the phonon lineshape and the characteristics of variable-temperature (85K to 600K) Raman spectra, we have determined quantitatively the third-order anharmonic phonon coupling matrix elements. The obtained values are noticeably lower than those reported in bulk ZnO, and we suggest isotope effects in Zn diffusion through Au nanocatalysts as a possible contributing mechanism.
ZnO nanowires (with diameters of ~ 30nm) were grown using a catalytic vapor-phase transport method with Au nanoparticles as the catalyst (details can be found in Ref.30). Micro-Raman spectra were obtained using a Renishaw InVia Raman microscope with the laser excitation provided by 325nm and 442nm lines from a Kimmon He-Cd laser. For measurements at temperatures from 85K to the room temperature (RT), we used a liquid-helium microscopy cryostat (part of CryoView2000 from Nanonics); high-temperature experiments (up to 600K) were performed using an Instec microscope hot stage (HCS302).

Transmission electron micrographs of a typical ZnO nanowire are shown in Figure 4.1. A residual catalyst can be seen at the tip of the nanowire, consistent with the catalyzed growth. The obtained electron-diffraction patterns indicate a wurtzite structure with [0002] as the growth direction. No dislocations or planar defects were observed from nanowires investigated.
Figure 4.2 (b) shows a RT Raman spectrum of the $E_2^{\text{high}}$ phonon (solid lines), which exhibits an asymmetric low-frequency broadening. This has been observed in bulk ZnO and attributed to anharmonic phonon interactions. While the isotopic disorder can also lead to such a broadening, it seems unlikely to be the origin here as the $E_2^{\text{high}}$ phonon mode involves predominantly the motion of oxygen atoms (which are nearly isotopically pure). Moreover, the $A_1$ longitudinal optical phonon peak (not shown here) exhibits a fairly symmetric lineshape,

![Graph](image)

Figure 4.2: (a) $\Gamma(\omega)$ [black solid lines] with $|V_3^+|^2$ and $|V_3^-|^2$ of 18 and 3 cm$^{-2}$, respectively (see also the text), and calculated $\Delta(\omega)$ [red dashed lines] from the Kramers-Kronig relation; (b) experimental Raman spectrum of the $E_2^{\text{high}}$ phonon (solid lines), with $\Gamma(\omega)$ and $\Delta(\omega)$ plotted as dashed lines; (c) simulated Raman lineshapes with $|V_3^+|^2$ of 18 cm$^{-2}$ (solid lines) and 28 cm$^{-2}$ (dashed lines), with $|V_3^-|^2$ of 3 cm$^{-2}$ in both cases, together with the experimental Raman lineshape (open circles).
excluding the lattice disorder as the dominant origin of the asymmetric broadening. This asymmetric lineshape of the $E_2^{\text{high}}$ phonon thus provides an opportunity to evaluate the anharmonic phonon coupling strength. In particular, the $E_2^{\text{high}}$ phonon decays anharmonically into two acoustic phonon modes at $\omega_1 = 250 \text{ cm}^{-1}$ and $\omega_2 = 190 \text{ cm}^{-1}$, as well as into a difference between an optical phonon and an acoustic phonon at $\omega_3 = 550 \text{ cm}^{-1}$ and $\omega_4 = 110 \text{ cm}^{-1}$, respectively.\textsuperscript{109, 111} This anharmonic phonon coupling changes the harmonic phonon frequency $(\omega_0)$ into a damped frequency $\omega$, with $\omega = \omega_0 + \Delta(\omega) + i\Gamma(\omega)$, where the term of $\Delta(\omega) + i\Gamma(\omega)$ is the phonon self-energy. The imaginary part of the phonon self-energy, $\Gamma(\omega)$, is given by\textsuperscript{112}

$$\Gamma(\omega) = |V_3|^2 \rho_{+}^{(2)}(\omega)[1 + n(\omega_1) + n(\omega_2)] + |V_3|^2 \rho_{-}^{(2)}(\omega)[n(\omega_4) - n(\omega_3)],$$

(4.1)

where $n(\omega)$ are Bose-Einstein occupation factors, $\rho_{+}^{(2)}(\omega)$ and $\rho_{-}^{(2)}(\omega)$ are the two-phonon sum and difference density of states (DOS), $|V_3|^2$ and $|V_3|^2$ are third-order anharmonic phonon coupling matrix elements for the decay into phonon sums and differences, respectively. The real part of the phonon self-energy, $\Delta(\omega)$, is related to $\Gamma(\omega)$ via the Kramers-Kronig transformation,

$$\Delta(\omega) = -\frac{2}{\pi} \mathcal{P} \int_{0}^{\infty} \frac{\omega' \Gamma(\omega')}{\omega'^2 - \omega^2} d\omega',$$

(4.2)

where $\mathcal{P}$ is the Cauchy principle value.

To evaluate the phonon self-energy, we used the two-phonon sum DOS reported in Ref. 111. We shifted the DOS by $+10 \text{ cm}^{-1}$, as done in Refs.\textsuperscript{78} and 111 for bulk ZnO, to compensate the errors in the \textit{ab initio} calculations. For the two-phonon difference DOS, we used a constant value of 0.25 cm$^{-1}$ (Ref.109), as the DOS is almost flat in the frequency region of interest ($400 - 460 \text{ cm}^{-1}$).

Figure 2.2 (a) shows the plot of $\Gamma(\omega)$ [solid lines] at RT calculated from Eq. (4.1), with $|V_3|^2$ and $|V_3|^2$ given by 18 cm$^{-2}$ and 3 cm$^{-2}$, respectively (see also below). A numerical algorithm was then
used to calculate \( \Delta(\omega) \) [dashed lines in Figure 4.2 (a)] via Eq. (4.2). The lineshape of the Raman peak is then given by

\[
I(\omega) \propto \frac{\Gamma(\omega)}{\Gamma(\omega)^2 + [\omega_0 + \Delta_0 + \Delta(\omega) - \omega]^2},
\]

where \( \Delta_0 \) is the frequency shift due to the lattice thermal expansion:

\[
\Delta_0 = -\omega_0 \gamma \int_0^T [\alpha_\parallel(T') + 2\alpha_\perp(T')] dT',
\]

with \( \parallel(T) \), and \( \perp(T) \) being the Grüneisen parameter (=2.02)\(^{111} \) the linear thermal expansion coefficients parallel and perpendicular to the \( c \) axis, respectively. For \( \parallel \) and \( \perp \), we used the values from Refs.\(^{113} \) and \(^{114} \) that extend from 90K to 400K, and we extrapolated these values to the 80-600K temperature regime.

The width of the Raman peak is determined, to a large extent, by \( \Gamma(\omega) \). The asymmetric broadening is the result of the strong frequency dependence of \( \Gamma(\omega) \) in the low-frequency tail region of the phonon peak, as shown in Figure 4.2 (b). Using Eqs. (1) - (4), we simulated the Raman lineshape, with \( |V_3^+|^2 \) and \( |V_3^-|^2 \) as the two varying parameters. To account for the finite width of instrument response of \( \sim 2 \text{ cm}^{-1} \), we have added this value to \( \Gamma(\omega) \) during the simulation. The results, for \( |V_3^+|^2 = 18 \text{ cm}^{-2} \) and \( |V_3^-|^2 = 3 \text{ cm}^{-2} \), were plotted as the solid line in Figure 4.2 (c) that agrees well with the experimental Raman peak (open circles). Similar analysis performed on bulk ZnO\(^{78} \) has yielded \( |V_3^+|^2 \approx 39 \text{ cm}^{-2} \) and \( |V_3^-|^2 \approx 4 \sim 6 \text{ cm}^{-2} \). Values of 29 cm\(^2 \) for \( |V_3^+|^2 \), and 3 cm\(^2 \) for \( |V_3^-|^2 \), have been obtained\(^{109} \) on bulk ZnO via the relationship between the phonon linewidth and isotopic composition. While there is an agreement on the value of \( |V_3^-|^2 \), the obtained value here for \( |V_3^+|^2 \) is significantly lower than those reported in bulk ZnO. We note that, as \( \rho^{(2)}(\omega) \) is assumed to be a constant, \( |V_3^+|^2 \) mainly determines the symmetric
broadening of the phonon peak, while larger values of $|V_3^+|^2$ indicates a larger degree of asymmetric broadening. To illustrate the significance of $|V_3^+|^2$, we simulated the Raman lineshape [dashed lines in Figure 4.2 (c)] using $|V_3^+|^2$ of 28 cm$^{-2}$, the lower end of the values reported in bulk ZnO. Obviously, the simulated lineshape with $|V_3^+|^2$ of 28 cm$^{-2}$ overestimates the asymmetric broadening of the $E_{2}^{\text{high}}$ phonon peak observed in ZnO nanowires.

To further verify the obtained values for $|V_3^+|^2$ and $|V_3^-|^2$, we calculated the peak position and the Raman linewidth as functions of temperature from equations above, using the same values for $|V_3^+|^2$ and $|V_3^-|^2$. For the comparison to the experiments, we note that the measured full width at half maximum ($\Gamma_{\text{FWHM}}$) is not simply $2\Gamma(\omega)$, but is given by\textsuperscript{112}

$$\Gamma_{\text{FWHM}} = \frac{2\Gamma(\omega_m)}{1 - \frac{d\Delta(\omega)}{d\omega}|_{\omega=\omega_m}}, \quad (4.5)$$

where $\omega_m$ is the center frequency of the Raman peak. The calculated results (dashed lines) fit well the experimental data (open circles) plotted in Figure 4.3. This validates the values of $|V_3^+|^2$ and $|V_3^-|^2$ obtained via the Raman lineshape analysis.
The low value of $|V_3|^2$ obtained here suggests a weaker asymmetric phonon line broadening and thus a suppressed anharmonic phonon coupling in ZnO nanowires than in bulk ZnO. Given the diameter (~30nm) of these nanowires, phonon confinement effects are not expected. In addition, Raman spectra of nanowires with diameters ranging from 20 to 80nm (not shown here) exhibit no noticeable difference. Thus the size effect seems unlikely to be the origin. On the other hand, we note that the frequency of the two-phonon sum DOS $[\rho_+^{(2)}(\omega)]$ is inversely proportional to the Zn atomic mass. During the ZnO nanowire growth via a catalytic process (a vapor-liquid-solid growth), Zn atoms in the vapor phase are transported to the growth substrate and then diffuse through Au nanocatalysts before reacting with the oxygen. This process might lead to a preferred

Figure 4.3: Frequency (a) and linewidth (b) of the $E_{2}^{\text{high}}$ phonon peak as functions of temperature. Open circles and dashed lines are experimental and calculated results (see also the text), respectively. Inset to (a) shows the normalized Raman spectra obtained, from top, at 85K, 320K, 440K, and 438K, with spectra shifted vertically for clarity.
Zn isotopic composition (e.g. via isotope effects in intermetallic diffusion\textsuperscript{115}) that is different than that of bulk ZnO. The resulting change in the magnitude (and the frequency dependence) of $\rho_4^{(2)}(\omega)$ in the frequency region of the $E_{2}^{\text{high}}$ phonon might account for the suppressed anharmonic phonon coupling. Further investigations are required to elucidate the underlying mechanisms.

In conclusion, via detailed analysis of the Raman lineshape, we quantitatively determined the values of third-order anharmonic phonon coupling matrix elements in ZnO nanowires. The validity of these determined values was confirmed by variable-temperature Raman characteristics. These values are noticeably lower than those reported on bulk ZnO, indicating a suppressed anharmonic phonon coupling in ZnO nanowires. This can have profound effects on the mechanical as well as thermal properties of these nanomaterials. The origin of such a suppression might lie in the isotope effects in Zn diffusion through Au nanocatalysts, a process during the vapor-liquid-solid growth; further investigation are needed to reveal the underlying mechanisms.
Chapter 5 Diameter Dependence of the Minority Carrier Diffusion Length in Individual ZnO Nanowires

Carrier transport in semiconductors is both fundamentally interesting and technologically relevant. Minority carrier transport is of special importance as it controls the majority carrier transport and the performance of p-n junction-based devices. A understanding of minority carrier transport properties, particularly the carrier mobility and diffusion length, is therefore critical to device modeling and development efforts. In semiconductor nanostructures, particularly semiconductor nanowires with diameters comparable to or smaller than the carrier diffusion length, surface effects play an important role in limiting carrier transport. The increasing significance of surface effects with the deceasing material dimension is commonly understood as a consequence of an increasing surface-to-volume ratio. As semiconductor nanowires have emerged as one of most powerful and versatile building blocks for novel device applications, a knowledge of carrier transport properties and surface effects in these nanomaterials is central to advancing many of the promising technologies.

Here we report the direct measurement of the minority carrier (holes in this case) diffusion length, $L_D$, in individual n-type ZnO nanowires, using a near-field scanning photocurrent microscopy technique (SPCM). The observed strong diameter dependence of $L_D$ provides important insight into surface effects. In particular, our results indicate a diameter-dependent surface electronic structure, particularly an increase in the density of mid-bandgap surface states with the decreasing nanowire diameter. This might be a universal phenomenon in wurtzite-type nanostructures, suggesting that besides the surface-to-volume ratio, possible changes in surface
electronic structures, as the material dimensions vary in the nanoscale regime, are critical in accounting for and understanding the effects of surfaces on various material properties.

ZnO nanowires were synthesized using a catalytic vapor-phase transport method (details can be found in Ref. 30). Nanowires with various diameters were obtained using gold colloids with different sizes under the same growth conditions. These nanowires, independent of the diameter, have wurtzite-type lattices with the growth direction along the [0002] direction and the side walls consisting of non-polar surfaces; no dislocations or planar defects were found by transmission electron microscopy measurements. The good crystal quality of these nanowires is also confirmed by the estimation of majority carrier mobility\textsuperscript{121} (see appendix A) as well as Raman spectra,\textsuperscript{31} where the main phonon (E\textsubscript{2}\textsuperscript{high} mode) peak width (~ 8 cm\textsuperscript{-1}) is comparable to that (~ 6 –7 cm\textsuperscript{-1}) in high-quality ZnO single crystals.\textsuperscript{78} For device fabrications, nanowires were dispersed in isopropanol alcohol and then drop-casted on heavily-doped silicon substrates coated with a 400 nm silicon nitride layer. Both Schottky and Ohmic contacts on single nanowires (i.e. Schottky diodes) are required for obtaining $L_D$ using the SPCM technique (see also below). Schottky diodes on single nanowires were fabricated using electron-beam lithography followed by oxygen plasma cleaning, metallization, and lift-off, with Schottky- and Ohmic contacts formed by the evaporation of Pt and Ti/Au, respectively. These devices exhibit rectifying current-voltage characteristics (see appendix A), as expected.

The SPCM measurements were implemented on a near-field scanning optical microscope (NSOM) in ambient air at room temperature, with the schematic setup shown in Figure 5.1 (a). The 325 nm emission from a HeCd laser, chopped (at 1 kHz) and then coupled to NSOM probes
with nominal aperture sizes between 100 – 150 nm, was used to locally illuminate single ZnO nanowire devices. This above-bandgap local optical excitation leads to a photocurrent, the magnitude of which was recorded using the lock-in technique, simultaneously with the topography, as a function of the NSOM probe position. As the NSOM probe is raster-scanned over a device, a photocurrent map is obtained. This technique has been used to obtain $L_D$ in Si\textsuperscript{122} and CdS nanowires.\textsuperscript{123} Using NSOM as the platform, provides the beyond-diffraction-limit spatial resolution, beneficial for extracting short $L_D$ in direct-bandgap semiconductors such as ZnO.

The near-field photocurrent maps of a typical ZnO nanowire Schottky diode are shown in Figures 5.1 (b) and (c). A relatively uniform spatial distribution of photocurrent was observed under the forward-biased condition [Figure 5.1 (b)]. This is expected, as the Schottky diode is

Figure 5.1: (a) Schematics of the near-field SPCM technique; photocurrent map under (b) forward and (c) reverse biased conditions. The insets to (b) and (c) show the schematic diagrams of the Fermi level ($E_F$) as well as conduction and valence bands (CB and VB).
“turned on” and there is a uniform electric field along the nanowire. In contrast, when the Schottky diode is reversely biased, photocurrent can only be observed near the Schottky contact [Figure 5.1 (c)]. In this case, the absence of photocurrent along the nanowire is due to the negligible electric field in the nanowire channel region, as indicated by the $I-V$ characteristics. The Schottky contact, especially when reversely biased, however, induces a localized band bending in the nanowire close to the Schottky electrode. This band bending, as shown schematically in the inset to Figure 5.1 (c), collects the holes that, under the low-level injection condition (see appendix A), diffuse from the optical generation region under the NSOM probe. This carrier collection leads to the detected photocurrent. Only when the NSOM probe is within a short distance (comparable or smaller than the hole diffusion length) from the Schottky contact will such a photocurrent be detected. Therefore, the decay of the photocurrent, $I_p$, away from the

Figure 5.2: (a) Photocurrent map with the shaded region and the dashed line representing the Schottky electrode and the nanowire, respectively; (b) the photocurrent spatial profile (open circles) along the nanowire (the shaded region represents the Schottky diode) with the inset showing the semi-logarithmic plot; the solid line represents a fitting using a convoluted Gaussian-exponential function; (c) the cross-section photocurrent profile (open circles) taken perpendicular to the nanowire, with the solid line representing a Gaussian-peak fitting.
Schottky contact, can be used to extract $L_D$, particularly via a single exponential relation, $I_P \sim \exp (-x/L_D)$.\textsuperscript{125}

From a typical high-magnification photocurrent map shown in Figure 5.2 (a), the corresponding photocurrent spatial profile [open circles in Figure 5.2 (b)] however, exhibits non-single-exponential characteristics. This is due to the fact that the aperture size of the NSOM probe is comparable to $L_D$. To account for this, we approximated the optical field of the NSOM probe with a Gaussian function\textsuperscript{126} and used a convoluted Gaussian-exponential function [solid lines in Figure 5.2 (b)] to fit the spatial profile. In this case, the best fitting was obtained a Gaussian function with a full-width-at-half-maximum (FWHM) of ~ 260 nm was used and an $L_D$ of ~ 126 nm. This FWHM corresponds to the width of the optical field under the NSOM probe.\textsuperscript{127} This fitting procedure is validated by measuring the FWHM of the cross-section photocurrent spatial profile [taken perpendicular to the nanowire, Figure 5.2 (c)] fitted with a single Gaussian function. The obtained value of ~ 275 nm agrees reasonably well with the sum of the nanowire diameter (~ 30 nm in this case) and the width of the NSOM probe optical field (~ 260 nm), as expected. This fitting procedure allowed us to reliably measure $L_D$ significantly smaller than the NSOM probe size.

As $L_D$ is sensitive to surfaces, the diameter dependence of $L_D$ can shed light on how the surface effects affect the carrier transport in the nanoscale. Figure 5.3 shows $L_D$ (solid circles) as a function of nanowire diameter (which was measured from the topography images). A strong diameter-dependence of $L_D$ can be seen for nanowire diameters below 40 nm; above 40 nm, $L_D$ approaches the value of ~ 250 nm. The absence of the diameter-dependence for large-diameter (> 40 nm) nanowires indicates negligible surface effects. We note that, in bulk n-type ZnO with the electron concentration of $10^{14}$ cm\textsuperscript{-3} and $10^{18}$ cm\textsuperscript{-3}, $L_D$ of 440 nm (Ref.128) and 130 nm
(Ref.129), respectively, have been reported. Here, using the values of the electron mobility and the electrical conductivity, we estimated the electron concentration in ZnO nanowires to be \( \sim 2 - 3 \times 10^{17} \text{ cm}^{-3} \). As \( L_D \), in general, decreases with increasing doping levels, \( L_D \) (\( \sim 250 \text{ nm} \)) in large-diameter ZnO nanowires measured here corresponds approximately to the bulk value. This confirms the absence of surface effects, at least for hole transport, in ZnO nanowires with diameters beyond 40 nm.

![Graph image](image)

Figure 5.3: Measured \( L_D \) (solid circles) as a function of nanowire diameter. The black dotted-dashed line represent the model with a constant \( S (=10^3 \text{ cm s}^{-1}) \); the blue dashed lines represents the model with a diameter-dependent \( S \) (red solid line) shown in the inset plotted on a semi-logarithmic scale.

Surface effects are, however, significant for small-diameter (< 40 nm) nanowires, as \( L_D \) decreases with the decreasing diameter. For minority carriers, carrier recombination mediated by mid-bandgap surface states is the main mechanism that limits \( L_D \). This process can be described by a simple model (see appendix A), where the surface-mediated carrier recombination is described by the surface recombination velocity \( S \). The value of \( S \) appears to have the strongest effect on the diameter dependence of \( L_D \). Using a constant \( S \) for all diameters, which is commonly assumed in describing surface effects,\(^{49, 119, 122, 130}\) however, does not yield
satisfactory fittings (e.g. the black dotted-dashed line in Figure 5.3) to the data. Particularly, the
model with a constant $S$ significantly underestimates the diameter dependence of $L_D$, indicating
that an increasing surface-to-volume ratio alone cannot account for the observed surface effects.
On the other hand, if $S$ is allowed to vary as a function of nanowire diameter during the fitting
procedure, a good agreement between the model (blue dashed line) and data can be obtained. In
this case, the fitting procedure leads to a diameter-dependent $S$ that increases with decreasing
diameter (inset to Figure 5.3).

This diameter-dependence of $S$ suggests a diameter-dependent surface electronic structure (see
appendix A). In particular, as $S$ is given by $N\sigma v_{th}$ under the low-level injection condition,$^{131}$
where $N$ is the surface state density, $\sigma$ is the carrier capture cross section, and $v_{th}$ is the carrier
thermal velocity, our results indicate that $N$ and/or $\sigma$ increase with decreasing nanowire diameter.
For bulk ZnO, if the dangling atomic bonds on the non-polar surfaces are considered as the main
origin of surface states,$^{132}$ these surface states are resonant with the conduction and valence
bands$^{133-135}$ and thus do not contribute significantly to carrier capture/recombination processes.
In this case, negligible surface effects are expected, which is consistent with $L_D$ and $S$ obtained in
large-diameter (> 40 nm) ZnO nanowires. The significant increase in $S$ observed here with
decreasing diameter is then most likely due to an emergence of mid-bandgap surface states, the
density of which increases with the decreasing diameter. A recent theoretical study$^{136}$ has
suggested a significant extension of surface states into the bandgap as the nanowire diameter
decreases, due to the cyclic boundary conditions imposed by the identical side surfaces of
wurtzite-type nanowires; this change in the surface electronic structure becomes noticeable for
GaN nanowires when the diameter decreases from 80 nm to 40 nm. Our observations here seem
to be consistent with these theoretical results, although further studies, such as x-ray
photoelectron spectroscopy measurements on individual nanowires as a function of diameter, are needed to clarify the origin of this phenomenon.

In summary, we have directly measured the minority carrier diffusion length, $L_D$, in individual n-type ZnO nanowires using a near-field SPCM technique. The diameter-dependence of $L_D$ suggests negligible (significant) surface effects for nanowire with diameters larger (smaller) than 40 nm. Our results indicate a diameter-dependent surface electronic structure, particularly an increase in the density of mid-bandgap surface states with the decreasing diameter. This diameter dependence of the surface electronic structure might be a universal phenomenon in wurtzite-type nanostructures. Although further studies are required to clarify the origin of this phenomenon, our results demonstrate that, as the material dimension decreases in the nanoscale regime, besides the surface-to-volume ratio, possible changes in the surface electronic structure are critical in accounting for and understanding the effects of surfaces on various material properties.
Chapter 6 Diameter-Dependent Surface Photovoltage and Surface State Density in Single Semiconductor Nanowires

Charge carrier transport plays a central role in semiconductor-based device operations. The minority carrier transport is particularly important, as it controls the majority carrier transport and thus the current characteristics in p-n junctions, a fundamental element in many semiconductor devices including solar cells, photodetectors, light emitting diodes, and lasers. With the device dimension decreasing in the nanometer regime, surface effects become a significant factor in limiting carrier transport. In semiconductor nanowires, which are being extensively explored for photovoltaics and opto-electronics, surface effects on carrier transport are often manifested through carrier trapping and electron-hole recombination at surface states.

As the diameter decreases, this surface-facilitated carrier recombination becomes to dominate over the recombination process in the bulk, and thus limit the minority carrier lifetime and diffusion length. Carrier recombination at the surface is usually described by the surface recombination velocity, \( S \), which is proportional to the surface state density and the carrier capture cross section. \( S \) has been assumed to be a constant quantity independent of the nanowire diameter, and the increasing dominance of the surface effects on carrier transport has been commonly explained by the increasing surface-to-volume ratio as the diameter decreases.

Recent studies, including our own, however, have suggested that the surface-to-volume ratio alone significantly underestimates the significance of surface effects at small diameters. Particularly, the transition from bulk-limited to surface-limited carrier transport occurs over a narrow diameter regime (between 30 – 40 nm), which cannot be accounted for by only the
variations of the surface-to-volume ratio within this regime. Correspondingly, these studies indicate a diameter-dependent $S$, which was shown to increase with the decreasing diameter in Si and ZnO nanowires.\textsuperscript{31, 143} A study of the photoluminescence lifetime in ZnO nanowires also indicates a diameter-dependent $S$;\textsuperscript{141} although this was not explicitly pointed out. The origin of this diameter dependence of $S$ remains unclear. Here, using single-nanowire surface photovoltage measurements, we directly determine the surface barrier height in single n-type ZnO nanowires. By coupling these results to finite-element electrostatic simulations, we obtain the acceptor-type surface state density and the minority carrier surface lifetime as functions of the nanowire diameter. These results identify an important origin of the diameter-dependent $S$ and account for the abrupt transition from bulk-limited to surface-limited minority carrier transport as the diameter decreases. These findings are further supported by the measurement of bulk-limited minority carrier diffusion length in the presence of strong surface effects, which enables a direct view of the significance of surface effects as a function of diameter through a comparison to the surface-dependent minority carrier diffusion length.

ZnO nanowires were grown by a catalytic chemical vapor deposition (CVD) method, as described previously.\textsuperscript{30} Single-crystal wurtzite-structure nanowires were obtained, and no extended lattice defects were observed by transmission electron microscopy.\textsuperscript{31} The growth direction of these nanowires is along the [0001] direction.\textsuperscript{31} Nanowires with different diameters were obtained under same growth conditions, and thus no diameter dependence of the unintentional impurity incorporation was expected. These nanowires are unintentionally n-type doped, with an electron mobility of $\sim 90 - 100 \text{ cm}^2/\text{Vs}$ and an electron density of $\sim 10^{17} \text{ cm}^{-3}$ determined from electrical measurements.\textsuperscript{32} The electron mobility and density are comparable to those reported in high-quality CVD-grown ZnO nanowires.\textsuperscript{144-147} For surface photovoltage
measurements, ZnO nanowires were deposited on Si substrates coated with a 200 nm-thick Si₃N₄ layer, and e-beam lithography followed by metallization and lift-off processes were used to define metal electrodes on single nanowires. The surface potential of single nanowires was measured by scanning Kelvin probe force microscopy (KPFM) with the global optical excitation provided by the 325 nm emission from a He-Cd laser; these experiments were carried out in ambient air [schematics shown in Figure 6.1 (b)]. Cr/Pt coated probes (ATEC, Nanosensors) with the nominal radius less than 20 nm were used for the KPFM experiments; details can be found in Ref. 143. Three-dimensional finite-element electrostatic simulations (see also below for details) were implemented using a commercial software (Synopsys TCAD Sentaurus).

Figure 6.1: (a) Schematic cross-sectional band diagrams of a nanowire in the dark and under an optical illumination, with EFp representing the hole quasi-Fermi level under the optical illumination; (b) schematic experimental setup of the surface photovoltage measurements. CB and VB in (a) represent the conduction and the valence bands, respectively.

The origin of surface photovoltage (SPV) is illustrated in Figure 6.1 (a) for an n-type semiconductor nanowire under a low-level optical illumination. Specifically, acceptor-like surface states, when occupied by electrons, carry negative charges and induce the upward surface band bending. Under an above-bandgap optical excitation, negatively charged surface states capture the photogenerated holes (which are minority carriers in this case) and become neutral,
and this reduces the surface band bending. SPV is defined as the changes in the surface potential due to this optical illumination. When most of the surface states are neutralized, the surface band bending disappears; in this case, the SPV approaches the maximum value (i.e. photosaturation), which corresponds to the surface potential barrier height at equilibrium (in the dark). This approach to measuring the surface potential barrier height has been widely used in characterizing surface properties of various bulk and thin-film semiconductors.\textsuperscript{148-150} (see also appendix B for potential issues of this approach).

Figures 6.2 (b) and (c) show the surface potential maps of a ZnO nanowire in the dark and under the optical illumination, respectively. With the carrier lifetime in ZnO on the order of hundreds of ps, the maximum optical power density (~ 0.3 Wcm\textsuperscript{-2}) used in this study leads to a photogenerated free carrier concentration of ~ 10\textsuperscript{13} – 10\textsuperscript{14} cm\textsuperscript{-3}. This is much lower than the equilibrium electron density (~ 10\textsuperscript{17} cm\textsuperscript{-3}) in our ZnO nanowires, and thus corresponds to the low-level optical excitation condition. By considering the work functions of Pt (KPFM probe) and ZnO, the observed increase in the surface potential under the optical excitation, i.e. a positive SPV as shown in Figures 6.2 (b) and (c), indicates a decrease in the work function of the ZnO surface. This is consistent with a lowering of the upward surface band bending, as shown in Figure 6.1 (c).\textsuperscript{151} This surface band bending is due to the presence of acceptor-type surface states. We note that the interaction between chemisorbed oxygen molecules and ZnO surface atoms leads to acceptor-type surface states with the energy (\(E_s\)) at ~ 0.7 – 0.9 eV below the conduction band.\textsuperscript{152} In addition, intrinsic acceptor-type surface states have also been reported at energy levels of 0.38 – 0.5 eV above the valence band.\textsuperscript{25,153} Other surface adsorbates including hydrogen and hydroxyl groups can also play a role in surface state formation.\textsuperscript{154} Among these, the oxygen-induced surface states have been shown to be the dominant species in
ambient air, and thus will be the focus of this study. These acceptor-type states, usually occupied by electrons as their energy levels are below the Fermi level in n-type ZnO under equilibrium, can capture photogenerated holes and thus play an important role in limiting hole transport.

Figure 6.2: (a) Topography image of a ZnO nanowire attached to a metal electrode; surface potential maps of the nanowire (b) in the dark and (c) under the optical illumination; (d) measured surface photovoltage (SPV, solid circles) as a function of optical excitation intensity; (e) measured surface potential barrier (solid circles) height as a function of nanowire diameter. Dashed lines in (d) and (e) are spline smoothing curves showing the general trend as guide of the eye. Scale bar in (a) – (c): 0.5 µm.

The surface barrier height at equilibrium can be obtained from the SPV under photosaturation conditions. The SPV was measured away from the metal junction, where the SPV is constant along the nanowire. Figure 6.2 (d) shows the SPV (solid circles) as a function of the optical excitation intensity. A saturation of SPV towards ~ 0.23 V can be observed. We note that the photosaturation occurs under low-level optical excitations. This suggests that the direct modification, specifically the neutralization, of negatively charged surface states is the main mechanism for the observed SPV and photosaturation, as opposed to the screening of the surface charges by photogenerated carriers. As discussed above, the saturation value of SPV can be
taken as the surface barrier height under equilibrium. Using this approach, the surface barrier height was obtained in nanowires with various diameters, and the results (solid circles) are shown in Figure 6.2 (e). In general, the surface barrier height increases with the decreasing diameter. To relate this result to the surface state density, we calculated the surface barrier height as a function of surface state density, $N_s$, for various nanowire diameters. Particularly, the three-dimensional Poisson’s equation,

$$\nabla^2 \phi = -\frac{q}{\varepsilon}(p - n + N_D^+) \quad (6.1)$$

With the charge neutrality condition, we have

$$\int (p - n + N_D^+) dV = \int N_s^- dA \quad (6.2)$$

where $N_s^-$ is the density of the electron-occupied surface states, which carry negative charges. The left side of the Equation (6.2) represents the total positive volume charges inside the nanowire, with the right side of the equation as the total negatively-charged (electron-occupied) surface states on the nanowire surface. The surface states are assumed to be distributed uniformly on the nanowire surface. The negatively charged surface state density, $N_s^-$, is related to the density of the total surface states, $N_s$, the Fermi-Dirac statistics. Equations (6.1) and (6.2) were solved together with the charge continuity equations at equilibrium

$$\frac{1}{q} \nabla \cdot (q\mu_n n \vec{e} + qD_n \nabla n) = -\frac{1}{q} \nabla \cdot (q\mu_p p \vec{e} + qD_p \nabla p) = 0 \quad (6.3)$$

in a self-consistent manner.

Table I lists the material parameters used in the calculation. The electron and hole diffusivities, $D_n$ and $D_p$, are calculated as $(kT/q) \mu_n$ and $(kT/q) \mu_p$, respectively. A donor activation energy of 46
meV was used for the calculation; this value corresponds to hydrogen donors, the dominant shallow donor species in ZnO, and is also consistent with variable-temperature electrical measurements of ZnO nanowires. Fermi-Dirac statistics was used to calculate the free electron density, which is close to the effective density of states of the conduction band in ZnO (~ $3 \times 10^{18}$ cm$^{-3}$). For the simulations, the ZnO nanowire was encapsulated by ambient air [Figure 6.3 (a)], and the surface states were defined at the nanowire/air interface.

Figures 6.3 (b) and (c) show the calculated cross-sectional distributions of the electrostatic potential and free electron density in a 27 nm-diameter nanowire. In this case, $N_s$ and $E_s$ are $4.1 \times 10^{12}$ cm$^{-2}$ and 0.9 eV (which corresponds to chemisorbed oxygen-related surface states) below the conduction band, respectively. As expected, the presence of acceptor-type surface states leads to the surface band bending and depletion of electrons near the surface. With the surface barrier height as a function of $N_s$ obtained through the simulation, as shown in Figure 6.3 (d), the value of $N_s$ can be determined for the measured surface barrier height. We note that the uncertainly on $E_s$ does not affect the determination of $N_s$, as shown in Figure 6.3 (d) for $E_s$ of 0.7 eV and 0.9 eV. This is true if the value of $E_s$ is large than the measured surface barrier energy ($0.15 – 0.3$ eV), i.e. the surface state energy levels are significantly below the conduction band, because in this case the electron occupation of surface states is independent of surface band bending. For the 27 nm-diameter nanowire, the experimentally measured surface barrier height ($\sim 0.29$ V) corresponds to an $N_s$ of $4.1 \times 10^{12}$ cm$^{-2}$. As a verification of the simulation results, the average free electron density with the $N_s$ given by $4.1 \times 10^{12}$ cm$^{-2}$ was calculated to be $\sim 2 \times 10^{17}$ cm$^{-3}$ from Figure 6.3 (c). This agrees well with the value experimentally estimated from electrical measurements ($\sim 10^{17}$ cm$^{-3}$).
$N_s$ as a function of nanowire diameter, plotted as solid squares in Figure 6.3 (e), in general, shows an increase in $N_s$ as the diameter decreases. This identifies an important origin of the diameter dependence of $S$, which is given by $N_s \sigma v_{th}$, with $\sigma$ and $v_{th}$ being the carrier capture cross section and thermal velocity, respectively. Further insights into the role of the diameter
dependence of $N_s$ in surface effects on minority carrier transport can be obtained by considering the following relation:

$$\frac{1}{\tau_{\text{eff}}} = \frac{4\beta^2 D_p}{d^2} + \frac{1}{\tau_B} \quad (6.4)$$

with $\beta$ given by:

$$\beta J_1(\beta) = \frac{dS}{2D_p} J_0(\beta) \quad (6.5)$$

where $\tau_{\text{eff}}$ is the effective hole lifetime, $\tau_B$ is the hole lifetime in bulk ZnO, and $d$ is the nanowire diameter. The diameter dependence of $\tau_{\text{eff}}$ is the controlling factor for the hole diffusion length, $L_D$, which is given by $\sqrt{D_p \tau_{\text{eff}}}$. The first term on the right side of equation (6.3) can be considered as an effective lifetime controlled entirely by surface effects, i.e. the surface lifetime, $\tau_{\text{sur}} = \frac{d^2}{4\beta^2 D_p}$. With the known $N_s$ and $\sigma$ (which is given by $10^{-16}$ cm$^{-2}$ for oxygen-induced surface states$^{161}$), $\tau_{\text{sur}}$ can be calculated as a function of nanowire diameter, and the results are plotted as solid circles in Figure 6.3 (f). The corresponding $\tau_{\text{eff}}$ was then obtained from equation (6.3) with $\tau_B$ taken to be 150 ps$^{162}$ and is shown in Figure 6.3 (f). The relative significance of surface effects is indicated by the comparison between $\tau_{\text{sur}}$ and $\tau_B$: when $\tau_{\text{sur}}$ is smaller (larger) than $\tau_B$, the hole transport is limited by surface (bulk) effects. As shown in Figure 6.3 (f), $\tau_{\text{sur}}$ becomes smaller than $\tau_B$ at the diameter of ~ 35 nm, and this is consistent with the previously reported transition from bulk-limited to surface-limited carrier transport in the 30 – 40 nm diameter regime.$^{30}$
This diameter dependence of $N_s$ indicates changes in the surface electronic structure as the diameter varies. Theoretical studies\textsuperscript{163,164} have suggested an increase in the mid-bandgap surface states in wurtzite-structure nanowires and quantum wells as the diameter and well thickness decrease.\textsuperscript{163,164}

![Figure 6.4](image)

**Figure 6.4:** (a) Schematics of the measurement of bulk-limited $L_D$; (b) surface photovoltage (SPV, solid circles) spatial variations along a nanowire, with the shaded region representing the metal electrode and the dashed line representing the fitting using the equation (6.5); (c) bulk-limited (solid circles) and surface-dependent (open circles) $L_D$ as functions of nanowire diameter. The surface-dependent $L_D$ is re-plotted from Ref. 139.

Such a trend was attributed to the coupling of surface wave functions on identical surfaces, e.g. the six (1100) side surfaces in [0001] oriented nanowires. Particularly for wurtzite GaN nanowires, this effect was calculated to become significant as the diameter decreases below 40 nm. As shown by simulations reported in Ref. 107, ZnO nanowires with different diameters exhibit different atomic displacements on the surfaces due to surface reconstructions. This was used to explain a diameter dependence of the Young’s modulus in the diameter range of 20 nm to 80 nm. The difference in the surface atomic displacements might lead to different surface electronic structures. In addition, previous experimental studies have shown changes in the x-ray near-edge absorption spectra in ZnO nanowires with various diameters.\textsuperscript{165} While the exact nature of the changes in the surface electronic structure remains unclear, such changes are likely to
modify the interactions between chemisorbed oxygen and surfaces, leading to a diameter-dependent \( N_s \). We note that this diameter dependence of \( N_s \) might not be the only origin of the strong surface effects and the diameter-dependent \( S \). As an example, modifications to the carrier capture cross section as the diameter varies might also contribute. Further studies including surface photovoltage spectroscopy measurements on single nanowires will provide more insights.

The comparison between \( \tau_{\text{sur}} \) and \( \tau_B \), as well as the diameter dependence of \( \tau_{\text{eff}} \), shows that surface effects are minimal for diameters beyond 45 – 50 nm and are dominant for diameters smaller than 30 – 35 nm. This can be directly validated by measuring the bulk-limited \( L_D \). Specifically, under the above-bandgap global optical excitation, the negatively charged acceptor-type surfaces states become neutralized, as shown schematically in Figure 6.1. These hole-occupied surface states can no longer trap holes and facilitate the electron-hole recombination; therefore, the transport of the remaining free holes is limited by bulk-related processes. Figure 6.4 (a) shows the principle of measuring the bulk-limited \( L_D \) from the spatial variations of photogenerated free holes \( \Delta p \) under a global optical excitation. Particularly, a metal-semiconductor junction creates a gradient of \( \Delta p \) close to the space-charge region, which collects the holes. This gradient is characterized by a single exponential function \( \exp \left( -\frac{x}{L_D} \right) \), with \( L_D \) in this case limited by the bulk effects. This gradient of \( \Delta p \) can be related to the surface photovoltage (SPV) through the relation established in Ref. 167:

\[
\text{SPV} (x) = C_0 \times \ln \left[ 1 + \frac{\Delta p}{C_2} \right] = C_0 \times \ln \left[ 1 + \frac{C_1 \times \exp \left( \frac{-x}{L_D} \right) + \Delta p_0}{C_2} \right] \tag{6.6}
\]

where \( C_0, C_1, \) and \( C_3 \) are constants, and \( \Delta p_0 \) is the density of photogenerated free holes away from the space-charge region. The spatial variations of SPV close to the metal junction are
controlled by $L_D$. By fitting the SPV spatial profile close to the metal junction using equation (6.6), the bulk-limited $L_D$ can be extracted. One example is shown in Figure 6.4 (b).\textsuperscript{168} The comparison between bulk-limited and surface-dependent $L_D$, the latter of which was obtained by the near-field scanning photocurrent microscopy,\textsuperscript{32} is shown in Figure 6.4 (c). Consistent with the $\tau_{\text{eff}}$ being limited by bulk-related processes for large diameters, the surface-dependent $L_D$ (open circles) is similar to the bulk-limited $L_D$ (solid circles) for diameters larger than 40 nm. For smaller diameters, an increasingly large difference between these two types of $L_D$ points to more substantial surface effects. This evolution of the significance of the surface effects as a function of nanowire diameter agrees well with that indicated in Figure 6.3 (f).

In summary, we have used KPFM to determine surface barrier height through surface photovoltage measurements in single ZnO nanowires. By considering the oxygen-induced surface states, which are the dominant surface species in ambient air in ZnO nanowires, we have estimated the corresponding surface state density based on the surface barrier height and finite-element electrostatic simulations. In general, the surface state density increases with decreasing diameter; this finding identifies an important origin of the diameter dependence of surface recombination velocity. Through the determination of the carrier surface lifetime based on this result, we suggest that this diameter dependence of the surface state density contributes to the transition from bulk-limited to surface-limited carrier transport over a rather narrow diameter regime (30 – 40 nm). In addition, we have measured the bulk-limited minority carrier diffusion length, $L_D$, at various diameters, the comparison of which to the surface-dependent $L_D$ enables a direct view of the significance of surface effects as a function of diameter. Our results provide important insights into surface effects on carrier transport in semiconductor nanostructures, and emphasize the need to consider mechanisms beyond the commonly used surface-to-volume ratio,
e.g. possible modifications to the surface electronic structure, in understanding the significance of surface effects.

Table 1: ZnO parameters used for simulation.

<table>
<thead>
<tr>
<th>Bandgap</th>
<th>Dielectric constant (ε)</th>
<th>Electron (hole) effective mass</th>
<th>Electron (hole) mobility: µ_n (µ_p)</th>
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</thead>
<tbody>
<tr>
<td>3.33 eV</td>
<td>8.66</td>
<td>0.24 (0.8) m_0</td>
<td>100 (34) cm²/Vs</td>
</tr>
</tbody>
</table>
Chapter 7 Quantitative Heat Dissipation Characteristics in Current-Carrying GaN Nanowires

With the continued decrease of the feature size, accompanied by the increase in device and power density in integrated circuits, managing heat generation and dissipation at nanoscale becomes increasingly important to reliable circuit operations. The development of effective thermal management schemes, to a large extent, depends on an understanding of heat dissipation and transfer characteristics in individual devices. Recently, semiconductor nanowires have been extensively explored as active device elements in nanoscale electronics. In particular, group III-nitride nanowires have shown enormous potential in optoelectronic applications, such as light-emitting diodes and lasers. These devices often operate at high power levels. Elevated temperatures, due to Joule heating, can be detrimental to device performance. This issue might be more significant in nanowire-based devices due to reduced thermal conductivities. Therefore, a quantitative knowledge of heat dissipation and transfer characteristics in these nanowires, especially when they are configured as active current-carrying elements, is central to developing effective cooling schemes and achieving envisioned applications. From a more fundamental perspective, studies of these characteristics can provide insight into how one-dimensional phonon confinement modifies thermal transport properties of these nanowires.

The heat dissipation and transfer properties can be obtained by analyzing the spatial variations of temperature in the active device region. A recent study used a model based on photoluminescence as a function of temperature to calculate the temperature profile along large-diameter (> 200 nm) GaN nanowires. This approach provided useful information on nanowire thermal conductivity and thermal resistance at the wire-substrate interface; however, direct measurements of temperature variations at nanoscale are desirable for enabling unambiguous and
deeper insight into heat dissipation and transfer characteristics. In addition, the thermal resistance at the wire-electrode interface might also be significant in contributing to the overall heat dissipation; this is also important for standard nanowire thermal conductivity measurements using the suspension configuration, where the wire-electrode (contact) thermal resistance, often ignored, can lead to significant errors.\textsuperscript{178}

For the direct measurement of temperature spatial variations, several techniques have been demonstrated,\textsuperscript{179, 180} including scanning thermal microscopy (SThM),\textsuperscript{63} micro-Raman spectroscopy,\textsuperscript{181, 182} infrared imaging,\textsuperscript{183, 184} and laser reflectance thermometry.\textsuperscript{185, 186} Compared to the far-field optical techniques, SThM, usually implemented on atomic force microscopes (AFM) working in the contact mode, provides beyond-diffraction-limit spatial resolutions;\textsuperscript{64, 187} such capabilities are highly desirable for resolving temperature variations within individual nanoscale objects. Particularly, SThM with the spatial resolution of \(\sim 50 – 100\) nm has been applied to probing energy dissipation in Joule-heated carbon nanotubes;\textsuperscript{188} these results based on SThM alone allowed the evaluation of the thermal resistances at both material-substrate and material-electrode interfaces,\textsuperscript{188} although a knowledge of the nanotube thermal conductivity was required for the analysis.

Here, we have investigated quantitatively the heat dissipation and transfer characteristics in individual current-carrying GaN nanowires using SThM complemented by spatially resolved Raman spectroscopy. We focus on nanowires with small diameters (40 – 60 nm), where the phonon confinement effect is pronounced\textsuperscript{175, 176} and expected to play a critical role in thermal transport. By analyzing the directly measured temperature profiles along both substrate-supported and suspended nanowire devices, and combining SThM results with spatially resolved single nanowire Raman spectroscopy, we have quantified the relative contributions from wire-
substrate and wire-electrode heat transfer to the total heat dissipation, thermal resistance at the wire-substrate and wire-electrode interfaces, and nanowire thermal conductivity. Our results also provide insights into certain aspects of tip-sample heat transfer mechanisms, the understanding of which is critical to quantitatively interpreting SThM results and to advancing applications of SThM in probing thermal properties at the nanoscale. In addition, the approach of combining SThM and spatially resolved Raman spectroscopy, as demonstrated here, can be important in

Figure 7.1: Figure 1. (a) Schematics of the SThM experiments; (b) ac and (c) dc SThM images with the inset to (b) showing the measured ΔVth (solid circles) as a function of V_{rms} and the parabolic fitting (dashed line); (d) SThM images showing the “double-line”-like structure and (e) the corresponding profile across the nanowire; (f) SThM image obtained in vacuum (~10^{-6} Torr); (g) profiles of ambient and vacuum SThM images taken perpendicular to the nanowire.
bringing a quantitative understanding to heat dissipation and thermal transport in nanoscale devices.

Single GaN nanowire two-terminal devices were fabricated on silicon substrates coated with a silicon nitride (Si₃N₄) layer (~400 nm thick). The Si₃N₄ layer was chosen, since it is increasingly being used as the gate material in GaN-based field-effect transistors (FETs). As “hot spots” often develop under the gate in FET structures, a quantitative knowledge of the thermal transport across the GaN and Si₃N₄ interface, particularly the thermal boundary resistance, is of practical significance. Ti/Au electrodes (~1µm wide) were defined by e-beam lithography followed by metallization and lift-off. For suspended nanowire device fabrications, we followed the procedure described in Ref. 192.

SThM was performed on an AFM (CryoView 2000, Nanonics) using thermoresistive probes mounted on quartz tuning forks [schematics shown in Figure 7.1(a)] with a normal-force feedback mechanism. The intermittent contact mode was used, which was necessary to minimize the mechanical interaction between nanowires and the probe; this was especially important for studying suspended nanowire devices. The thermal probe consists of two Pt wires running through a glass fiber. The fused Pt wire junction, which protrudes out of the bottom of the fiber, acts as the heat sensor. With a small amount of current (0.05 mA) through the Pt wire junction, the change in the electrical resistance of this junction, obtained by measuring the voltage change across a Wheatstone bridge (ΔVth), corresponds to the temperature variations at the wire junction. The diameter of this junction ranges from 150 to 200 nm. While larger than the resolution (50 – 100 nm) that has been achieved with thermocouple probes, the measured temperature profile along nanowires (with the length of 4 – 8 µm) is expected to approximately reflect the temperature variations within nanowires. For spatially resolved single nanowire
Raman spectroscopy, the optical excitation provided by the 442 nm emission from a He-Cd laser (Kimmon), and an optical microscope coupled to a Raman spectrometer (Invia, Renishaw) was used to focus the laser beam to a diffraction-limited spot. An optical microscope hot stage (HCS302, Instec) was used to carry out variable-temperature Raman spectroscopy measurements.

Thermal images (without filtering or averaging) of a 40 nm diameter GaN nanowire device, under ac and dc biases, in ambient air, are shown in Figures 7.1 (b) and (c), respectively. In particular, for the ac bias condition, a sinusoidal voltage with a dc offset \( v = V_{DC} + V_{DC} \sin 2\pi ft \) (\( f = 500 \text{ Hz} \)) was applied across the device, and the thermal signal (\( \Delta V_{\text{th}} \)) was detected using the lock-in technique. To exclude the possibility of electrical coupling between the SThM probe and nanowires, we applied the same bias across the two electrodes, in which case no contrast was observed. Furthermore, \( \Delta V_{\text{th}} \) follows a parabolic relation to \( V_{\text{rms}} \) (the root-mean-square voltage of the ac bias), as shown in the inset to Figure 7.1(b), verifying that \( \Delta V_{\text{th}} \) is a measure of dissipated power and thus the temperature of the nanowire. This parabolic relation also indicates diffusive phonon transport, as expected, since the effective phonon mean free path in nanowires is usually comparable to the nanowire diameter.\(^{193, 194}\) While the dc image shows essentially the same temperature variations as the ac image, the noise level is much higher. We therefore conducted the rest of experiments using the ac bias mode. The close similarity between the dc and ac temperature profiles allowed us to use a steady-state analysis (see also below).

Before analyzing the temperature profiles along nanowires, we first would like to discuss several relevant aspects that are important to applying the SThM technique to nanowire thermal imaging. Particularly, it is well known that topographical features often lead to artifacts in thermal
images.\textsuperscript{63} Such artifacts appear to be negligible in the case of carbon nanotubes;\textsuperscript{188, 195} however, for semiconductor nanowires with diameters on the order of tens of nanometers, topography-related artifacts can be rather significant. Here, we have observed a “double-line”-like feature in all the thermal images, with one example shown in Figures 7.1(d) and (e). Specifically, a darker region (with a smaller $\Delta V_{th}$) is sandwiched between two brighter lines (with a larger $\Delta V_{th}$) in the perpendicular direction to the nanowire. We suggest that this is due to the triangular cross section of GaN nanowires: when the tip is on the top of the apex, the thermal coupling between the tip and the nanowire is rather poor compared to that when the tip is on one of nanowire facets, leading to a lower $\Delta V_{th}$. Measurements on nanowires without such a triangular cross section will further elucidate the nature of this feature and are currently underway. Nonetheless, the temperature profiles along the nanowire measured from these regions show the same spatial variations (not shown here), we thus used the averaged $\Delta V_{th}$ across the nanowire to represent the local temperature.

Another important aspect relevant to SThM imaging is the relative significance of various tip-sample heat transfer mechanisms, which plays an important role in determining the spatial resolution and is critical to quantifying SThM results. In particular, under ambient condition, heat conduction through air, a liquid film bridging the tip and the sample surface, and solid-solid contact, as well as the radiative heat transfer, are the possible mechanisms. It has been shown that,\textsuperscript{64, 196} for submicron-size features, liquid conduction is the dominant mechanism. A recent study\textsuperscript{189} demonstrated that, in addition to the liquid conduction, the solid-solid conduction also plays an important role. In these studies, air and radiative conductions were found to be negligible. Here, Figure 7.1(f) shows a SThM image under high vacuum ($\sim 10^{-6}$ torr). This can be directly compared to Figure 7.1(b), as both images were obtained under otherwise the same
conditions using the same thermal probe. It is obvious that, from Figure 7.1(g), a slow-varying background signal away from the nanowire, which is the heat source, is present in the ambient SThM image, whereas such a feature is absent in the vacuum. As the heat conduction through the air is relatively insensitive to the distance between the tip and the heat source,\textsuperscript{189} we suggest that this background signal is dominated by the air conduction between the SThM probe and the nanowire.\textsuperscript{197} For the thermal signal obtained directly on the nanowire, however, there is little difference ($\sim 5\%$) in the signal strength between the ambient and the vacuum images. This is in sharp contrast to previous studies,\textsuperscript{196} where the thermal signal was found to decrease more than an order of magnitude in vacuum ($\sim 10^{-5}$ torr), due to diminished liquid conduction. Since solid-solid and radiative conduction are the dominant heat transfer mechanisms in vacuum,\textsuperscript{198,199} our results suggest that, under ambient condition, these two processes also dominate the observed thermal signals.\textsuperscript{200} A potentially important implication of these results is that, for experiments conducted in ambient, while the air conduction deteriorates the lateral spatial resolution (perpendicular to the nanowire), the temperature variations along the nanowire should be mostly limited by the size of the thermal probe, as both solid-solid and radiative (in this case, most likely the near-field radiation) conduction are expected to be short-range interactions.\textsuperscript{201, 202} Therefore, although vacuum SThM has been suggested to yield higher spatial resolutions,\textsuperscript{203} the ambient SThM, at least in our case, is expected to achieve the same spatial resolution along the nanowire.

Next we discuss the quantitative aspects of thermal images. In substrate-supported devices, the temperature profile is relatively constant along the most part of the nanowire. For the quantitative analysis, we follow the model developed in Ref.188 Particularly, with one-dimensional diffusive heating at steady state, we have
\[ kA \frac{\partial^2 T(x)}{\partial x^2} + \frac{Q}{L} - G \times W \times [T(x) - T_0] = 0 \]  

(7.1)

where \( k, A, T(x), T_0, Q, L, G, W \) are the nanowire thermal conductivity, cross section area, local temperature on the nanowire, ambient temperature, total heating rate, device channel length, nanowire-substrate thermal conductance per unit area, and the width of the nanowire, respectively. The solution, with \( x = 0 \) at the middle of the channel, is given by

\[ \theta(x) = \frac{T(x) - T_0}{T_{avg} - T_0} \]

\[ = q \times \left[ 1 - \frac{\cosh(mx)}{\cosh\left(\frac{mL}{2}\right)} \right] + \frac{2(T_{e,1} - T_0) + (T_{e,2} - T_0)}{2(T_{avg} - T_0)} \times \frac{\cosh(mx)}{\cosh\left(\frac{mL}{2}\right)} \]

\[ + \frac{T_{e,2} - T_{e,1}}{2(T_{avg} - T_0)} \times \frac{\sinh(mx)}{\sinh\left(\frac{mL}{2}\right)}, \]

with \( q = \frac{Q}{L6W(T_{avg} - T_0)} \), and \( m = \sqrt[\frac{GW}{kA}} \).  

(7.2)

where \( T_{avg} \) is the average temperature along the nanowire, with \( T_{e,1} \) and \( T_{e,2} \) being the temperatures at the interface between nanowire and the two electrodes. The fitting of the measured temperature file using this relation, with \( q \) and \( m \) as the varying parameters, is plotted in Figure 7.2 (a). The inset shows the fitting to a temperature profile obtained on a short-channel (~ 5µm) device. The curvature of the temperature profile is controlled by \( m \), while \( q \) mostly determines the magnitude. From the values of \( q \) and \( m \), \( G \) and \( k \), the parameters of interest here, can be directly obtained if the absolute value of \( T_{avg} - T_0 \) is known. To obtain this value from
Figure 7.2: (a) Temperature ($\theta$) profiles (black solid lines) along nanowires and the fitting results (red dotted lines) using eq 7.2; (b) spatially resolved Raman spectra of the A$_1$ LO phonon mode with spectrum a taken under the zero-bias (power) condition and spectra b-d taken along the biased nanowire with positions indicated in the inset, and the spectra are shifted vertically for clarity; (c) frequency of the A$_1$ LO phonon mode measured (solid circles) on a single nanowire as a function of the ambient temperature with the red solid line representing the fitting result.

SThM images requires a quantitative knowledge of the thermal resistance at the tip-nanowire junction, which, as a convoluted function of sample surface and ambient condition (e.g. humidity) as well as sample topography, is very difficult to quantify. In Ref. 188, the values of previously measured carbon nanotube thermal conductivity were used to obtain $G$. Here, however, $k$ of GaN nanowires is unknown and is the parameter to be determined.

To address this issue, we used spatially resolved Raman spectroscopy for the direct measurement of $T_{avg} - T_\theta$ via lattice phonon modes. It is well known that the frequencies of the lattice phonons decrease with increasing temperature. Figure 7.2(b) shows Raman spectra of the A$_1$ longitudinal optical (LO) phonon mode taken from the various locations on the nanowire device.
channel. Particularly, compared to the spectrum (curve a) taken without any bias (i.e. without any Joule heating), the frequency of the $A_1$ LO phonon mode ($\omega_{LO}$) shifts to lower values when the nanowire is biased. Such a change was found to be uniform along most of the nanowire channel, consistent with SThM results.$^{207}$ We have also measured Raman spectra in nanowire channel regions right next to the electrodes (not shown here), and we observed a larger decrease in $\omega_{LO}$, indicating higher temperatures in these regions. This is in conflict with SThM results showing lower temperatures close to the electrodes. We believe that this is due to the optical absorption of laser energy by the metal electrodes, which leads to a temperature increase in the electrodes as well as the adjacent nanowire regions. This suggests that, while Raman spectroscopy can enable a direct measurement of temperature, it has limited capabilities in resolving temperature variations close to metal contacts, which contain important information on heat dissipation characteristics. To relate the shift in $\omega_{LO}$ to the temperature change, we carried out variable-temperature Raman on a single GaN nanowire. Figure 7.2(c) shows $\omega_{LO}$ measured (solid circles) at various temperatures. A model (see appendix C), which takes into account the thermal expansion, three-phonon and four-phonon anharmonic coupling processes, was used to fit [solid line in Figure 7.2(c)] $\omega_{LO}$ as the function of temperature. The obtained fitting parameters allow us to calculate the temperature from any shift in $\omega_{LO}$. With nanowire devices powered similarly (in the range of 100 – 400 $\mu$W) for SThM and Raman studies, we obtained $T_{avg} - T_0$ (ranging from ~ 35 – 120 K).$^{208}$

With this, we estimated $k$ to be ~ 50 – 60 W/mK and $G$ to be ~ 0.3 – 2.0 $\times$ 10$^7$ W/m$^2$K across various nanowire devices. For comparison, the $k$ of bulk GaN$^{209}$ depends on the doping level ($n_e$): with $n_e$ increasing from ~ $10^{17}$ to $10^{19}$ cm$^{-3}$, $k$ decreases from ~ 200 to 75 W/mK. In addition, a previous study,$^{175}$ which used the micro-heating technique with a suspended
configuration, measured $k$ of GaN nanowires (with diameters $> 97$ nm) to be $\approx 13 - 19$ W/mK. The low $k$ obtained was attributed to a large mass-difference scattering rate primarily due to the presence of Si impurity atoms.\textsuperscript{175} Here, with an estimated $n_e \approx 10^{18}$ cm$^{-3}$, the values of measured $k$ are below the corresponding bulk value ($\approx 110$ W/mK), possibly due to the phonon confinement and boundary scattering effects. While there is a likely presence of extended defects (e.g. stacking faults), as suggested for GaN nanowires growth by thermal CVD,\textsuperscript{210} such defects were shown to play a minor role in limiting the room-temperature $k$.\textsuperscript{175} On the other hand, these values of $k$ are higher than those obtained in larger-diameter GaN nanowires.\textsuperscript{175} This could be due to a lower $n_e$ as a result of the absence of Si impurity atoms (assuming that the origin of these impurities is the Si substrates used for nanowire growth\textsuperscript{211}), which are donors in GaN, as well as a weaker mass-difference scattering. With regard to $G$, while there is no literature results for the GaN/$\text{Si}_3\text{N}_4$ interface, the values obtained here ($\approx 0.3 - 2.0 \times 10^7$ W/m$^2$K) fall into the range of those determined for GaN/Si ($\approx 1.4 - 3.0 \times 10^7$ W/m$^2$K),\textsuperscript{212,213} GaN/SiC ($\approx 0.8 - 3.0 \times 10^7$ W/m$^2$K),\textsuperscript{212,213} and GaN/sapphire ($\approx 0.2 - 1.0 \times 10^7$ W/m$^2$K) interfaces.\textsuperscript{213-215}

Based on the fitting results and the obtained $k$ and $G$, we next discuss the heat dissipation in GaN nanowires. The rate of heat dissipated from the nanowire into two metal electrodes, $Q_e$, can be written as\textsuperscript{188}

\[
Q_e = \frac{2}{Q} \left[ 1 - \frac{(T_{e,1} - T_0) + (T_{e,2} - T_0)}{2(T_{avg} - T_0)q} \right] \times \tanh \left( \frac{mL}{2} \right) 
\]

This ratio, in general, decreases (from $\approx 20\%$ to $\approx 7\%$) with increasing nanowire channel length (from 4 to 8 $\mu$m). In any case, this rather small ratio suggests that the majority of the heat is transferred out of the nanowire into the substrate, although for shorter-channel devices, the heat
transfer into the electrodes might begin to play a more important role. This heat dissipation characteristic can be understood from the thermal resistances at the wire-substrate \((R_{i,s})\) and wire-electrode \((R_{i,e})\) interfaces. In particular, \(R_{i,e}\) is given \(^{188}\) by \(((T_{e,1} - T_0) + (T_{e,2} - T_0))/Q\), and, on average, was estimated to be \(\sim 4 \times 10^6\) K/W. \(R_{i,s}\) can be obtained directly by \(1/GWL\), and is in the range of \(0.5 - 1.1 \times 10^6\) K/W. As \(R_{i,e}\) is larger than \(R_{i,s}\), more heat is dissipated through the substrate. We note that both \(R_{i,e}\) and \(R_{i,s}\) are much smaller than the nanowire thermal resistance, \(R_{nw}\), given by \(L/kA\), which is on the order of \(10^8\) K/W.

Figure 7.3: (a) Schematics of the suspended nanowire device; (b) spatially resolved Raman spectra of the Al LO phonon mode with the spectrum a taken under the zero-bias (power) condition and spectra b and d taken along the biased nanowire with positions indicated in (a), and the spectra are shifted vertically for clarity; (c) the topography profile (\(\Delta h\)) along the suspended nanowire with the height of the nanowire subtracted, and the inset shows the corresponding SThM image; (d) the temperature profile (black solid line) of the SThM image shown in the inset to (c) with the red dotted lines representing the fitting results using eq 7.4.
To further illustrate the dominant role of the wire-substrate heat dissipation, we conducted studies on suspended nanowire devices. We note that the suspended geometry corresponds to the configuration of fin-type field effect transistors (FinFET).\textsuperscript{171, 216} Due to the gravity, suspended GaN nanowires are curved, and the mid-section of the nanowire is in contact with the substrate, as illustrated in Figure 7.3(a). This is confirmed by the AFM topography profile along the suspended nanowire [Figure 7.3(c)]. The SThM image [inset to Figure 7.3(c), with the temperature profile shown in Figure 7.3(d)] of this suspended device shows completely different temperature variations than those of substrate-supported devices. Particularly, the temperature is lowest in the region when the nanowire makes contact with the substrate, and the highest temperature is in the middle of the suspended section. This is also confirmed by spatially resolved Raman studies with the spectra shown in Figure 7.3(b). The relative significance between wire-substrate and wire-electrode heat dissipation can be seen from the temperature difference at these two interfaces. Consistent with the analysis on substrate-supported nanowires, the lower temperature at the wire-substrate contact region, compared to that at the wire-electrode interface, clearly demonstrates the dominant role of the former in dissipating heat.\textsuperscript{217} This sample geometry also allows an estimation of the nanowire thermal conductivity. In particular, with $G = 0$ for the suspended section, the solution to eq. (7.1), with the left electrode at $x = 0$, is given by

$$
\theta(x) = \frac{T(x) - T_0}{T_{avg} - T_0} = -\frac{Q}{2kA(T_{avg} - T_0)l}x^2 + \left[\frac{Q}{2kA(T_{avg} - T_0)} + \frac{T_{e,2} - T_{e,1}}{(T_{avg} - T_0)l}\right]x + \frac{T_{e,1} - T_0}{T_{avg} - T_0} \quad (7.4)
$$
Using the same approach (with spatially resolved Raman spectra) as in the previous analysis for determining $T_{\text{avg}} - T_0$, the fitting of the temperature profiles yields $k$ of $\sim 40 - 45$ W/K, in reasonable agreement with the results obtained on substrate-supported devices.218

In summary, using the SThM technique combined with spatially resolved Raman spectroscopy, we provided a quantitative analysis of heat dissipation characteristics in typical operating GaN nanowire devices with the channel length of 4 – 8 µm. In particular, for substrate-supported GaN devices, we have quantitatively determined the wire-substrate and wire-electrode thermal resistances ($\sim 0.8 \times 10^6$ K/W and $4 \times 10^6$ K/W, on average, respectively) with the wire-substrate thermal conductance per unit area estimated to be $\sim 0.3 - 2.0 \times 10^7$ W/m²K, as well as the thermal conductivity ($50 - 60$ W/mK) of GaN nanowires with small diameters (40 – 60 nm), in which the phonon confinement effect is expected to be significant. Consistent with the smaller wire-substrate thermal resistance than that of the wire-electrode interface, the majority of the heat ($7 - 20\%$) generated in the nanowire is dissipated into the substrate. Analysis of suspended nanowire devices further demonstrated the significance of wire-substrate interface in total heat dissipation. These quantitative heat dissipation characteristics are important for designing efficient thermal management schemes for nanowire devices. In addition, the approach combining SThM and spatially resolved Raman spectroscopy, as demonstrated in this study, can play an important role in establishing a quantitative understanding of heat dissipation and transfer in various nanoscale devices.
Chapter 8 Appendices

A. Supporting Information for SPCM

Current-voltage characteristics of ZnO nanowire devices

The current-voltage (I-V) characteristics of a typical Ohmic device (with two Ti/Au contacts) are shown in Figure A.1(a). The linear I-V curve is consistent with the Ohmic nature of the Ti/Au contacts. The transfer characteristics [inset to Figure A.1(a)], with the heavily-doped silicon substrate as a back gate, show that the drain current (I_D) increases with an increasing drain-source voltage (V_{DS}). This indicates that these as-grown ZnO nanowires are n-type (unintentionally doped). The electron (majority carriers) field-effect mobility of \( \sim 100 \) cm\(^2\)/Vs was extracted from the transfer curve using the cylinder-on-plate model\(^{219}\). Measurements on a number of devices yielded mobility values between 90 and 100 cm\(^2\)/Vs, comparable to those reported for high-quality ZnO thin films\(^{220,221}\) and as-grown nanowires\(^{19,144}\).

The single nanowire Schottky diode shows rectifying current-voltage (I-V) characteristics [Figure A.1(b)], as expected. The current under the reverse-biased condition (where the Schottky contact is negatively biased) is below the resolution of the measurement circuit (\( \sim 1 \) pA). This suggests negligible electric field in the nanowire channel.

Figure A.1: I-V characteristics of (a) an Ohmic device and (b) a Schottky diode. The scanning electron microscopy images of the corresponding devices are shown in the inset.
region under the reverse-biased condition, a prerequisite for obtaining the diffusion length using the SPCM technique (see also the text).

**Verification of the low-level injection condition**

The verification of the low-level injection condition, in most cases, requires an estimate of the optical excitation power. However, it is rather difficult to measure the laser power in the near-field region of NSOM probes. Here we use a different approach based on the photocurrent map obtained under the forward-biased condition [e.g. Figure 5.2 (b) in the text]. In particular, we divide the nanowire into small segments (Figure A.2), with the length of each segment given by the diameter ($a$) of the NSOM probe.

The single nanowire Schottky diode shows rectifying current-voltage (I-V) characteristics [Figure A.2(b)], as expected. The current under the reverse-biased condition (where the Schottky contact is negatively biased) is below the resolution of the measurement circuit ($\sim 1$ pA). This suggests negligible electric field in the nanowire channel region under the reverse-biased condition, a prerequisite for obtaining the diffusion length using the SPCM technique (see also the text).

![NSOM Probe Diagram](image)

Figure A.2: Schematics for the estimation of the carrier injection level under local illumination via an NSOM probe.
We write, assuming \( n_0 \gg p_0 \) (which is valid in n-type semiconductors),

\[
\begin{align*}
\frac{1}{r_0} &= \frac{1}{q(n_0 \mu_n + p_0 \mu_p)} \\
&\approx \frac{1}{q n_0 \mu_n} \\
\end{align*}
\]  
(A.1)

where \( r_0 \) is the equilibrium resistance of the small segment, \( n_0 \) \((p_0)\) is the equilibrium electron (hole) density, and \( \mu_n \) \((\mu_p)\) are the electron (hole) mobility. The total resistance of the nanowire \((R_0)\) is then given by

\[
R_0 = r_0 \times \left( \frac{L}{a} \right)
\]  
(A.2)

where \( L \) is the total length of the nanowire. Under the illumination from the NSOM probe, the resistance of the segment directly under the NSOM probe decreases due to the increase in the local densities of electrons and holes, \( \Delta n \) and \( \Delta p \), respectively. Here we assume that \( \Delta n = \Delta p \). The resistance then becomes \( r \), which is given by

\[
r = \frac{1}{q(\Delta n + n_0) \mu_n + \Delta p \mu_p)}
\]  
(A.3)

This change in the resistance is confined to one segment; the resistance of other segments is still \( r_0 \). In this case, the total resistance of the nanowire becomes \( R \), which is given by

\[
R = r + r_0 \times \left( \frac{L}{a} - 1 \right)
\]  
(A.4)

As \( R > R_0 \), under a constant external bias \( V \), there is an increase in the current, i.e. the photocurrent current \( I_p \). We write

\[
I_0 + I_p = \frac{V}{R}
\]  
(A.5)
with

\[ I_0 = \frac{V}{R_0} \]  \hspace{1cm} (A.6)

Then we have, from the equations above

\[ \frac{I_0 + I_P}{I_0} = 1 + \frac{I_P}{I_0} = \frac{R_0}{R} = \frac{L/a}{1 + \frac{\Delta n/\mu_n}{\mu_p} + \frac{\Delta \mu}{\mu_p}} \]  \hspace{1cm} (A.7)

\( I_P \) and \( I_0 \) were measured to be ~ 0.5 nA on average and ~ 3 μA, respectively, under the forward bias condition (\( V = 3V \)). With the nanowire channel length of 7 μm and the NSOM aperture size of 200 nm, we calculated \( \Delta n/n_0 \) to be ~ 0.3% if \( \mu_n = \mu_p \) and ~ 0.6% if \( \mu_p = 0 \). As \( \mu_p \) is usually smaller than \( \mu_n \) but larger than zero, \( \Delta n/n_0 \) is between 0.3% and 0.6% under current experimental conditions, and this verifies the low-level injection condition.

**Model of \( L_D \) as a function of nanowire diameter**

\( L_D \) is equal to \( (D \tau_{\text{eff}})^{1/2} \), where \( D \) and \( \tau_{\text{eff}} \) are the diffusion constant (=\( k_B T \mu_p/q \), with \( \mu_p \) as the hole mobility) and the effective lifetime of holes, respectively, the surface-mediated carrier recombination leads to a decrease in \( \tau_{\text{eff}} \) and thus \( L_D \). This process can be described by a simple model.\(^{49, 222}\) Assuming an infinitely long cylindrical geometry, the continuity equation is:

\[ \frac{\partial (\Delta p)}{\partial t} = D \nabla^2 (\Delta p) - \frac{\Delta p}{\tau_B} \]  \hspace{1cm} (A.8)

where \( \Delta p \) is the photogenerated hole density, \( r \) is the radial coordinate, and \( \tau_B \) is the hole lifetime in bulk ZnO, with the boundary condition given by

\[ D \frac{\partial (\Delta p)}{\partial r} \bigg|_{r=\frac{d}{2}} = -S \Delta p \]  \hspace{1cm} (A.9)
where \( d \) is the nanowire diameter and \( S \) is the surface recombination velocity. The continuity equation can be solved analytically, leading to

\[
\frac{1}{\tau_{\text{eff}}} = \frac{4\beta^2 D}{d^2} + \frac{1}{\tau_B}
\]  

(A.10)

where \( \beta \) is given by:

\[
\beta J_1(\beta) = \frac{dS}{2D} J_0(\beta)
\]  

(A.11)

with \( J_{0,1}(\beta) \) as the Bessel functions (which are of the first kind) of zero and first order, respectively. With \( \tau_B \) taken as 970 ps (Ref. 223) and with the assumption of \( D \) being constant over different diameters,\textsuperscript{224} we modeled \( L_D \) as a function of nanowire diameter (Figure 5.3).

B. Supporting Information: Diameter-Dependent Surface Photovoltage and Surface State Density in Single Semiconductor Nanowires

There are several scenarios that can lead to false results regarding the determination of the surface barrier height using the surface photovoltage approach, according to Ref. 153 (Aphek, et al., Surf. Sci. \textbf{1998}, 409, 485-500). First of all, the photo-Dember electric potential, which arises from the spatial separation of photogenerated electrons and holes as a result of different electron and hole mobilities, can lead to significant errors. However, as discussed in the note (Ref. 148), this effect requires high-level injection conditions and therefore is not expected to play a significant role in our case.

Another potential concern, according to Ref. 153, is that, if the quasi-Fermi level of electrons or holes varies significantly through the surface depletion region under the optical illumination, then the surface photovoltage might reach a false saturation that does not correspond to the
surface barrier height. For the quasi-Fermi level to remain constant through the surface depletion region, two criteria must be satisfied: (1) the carrier diffusion length needs to be larger than the surface depletion region; and (2) the recombination current inside the surface depletion region needs to be small. The former criteria is satisfied in our case, since the carrier diffusion length is significantly larger than the nanowire diameters, as shown in Figure 6.4 (c). The 2nd criterion can be evaluated via the gradient of the quasi-Fermi level (Ref. 153), where $F_p$, $N_s$, and $\mu_p$ are the hole quasi-Fermi level, surface state density, and hole mobility, respectively, with $c_p$ given by the production of capture cross $\sigma$ and thermal velocity $v_p$. While this equation was derived for the one-dimensional case, it should yield an order-of-magnitude estimate for our case. If $\Delta F_p$ is small, then the 2nd criterion is satisfied (Ref. 153). Taking $N_s$ of 1013 cm$^{-2}$, $\sigma$ of $10^{-16}$ cm$^2$ (for oxygen-induced surface states), and $\mu_p$ of 34 cm$^2$/Vs, $\left| \frac{dF}{dx} \right|$ can be estimated to be $\sim 380$ V/cm. With a surface depletion region of $\sim 8$ nm [e.g. Figure 6.3 (c) in the text], we obtain $\Delta F_p \sim 0.3$ meV. This value is much lower than $kT$ ($\sim 26$ meV) at room temperature, and is therefore negligible.

In addition, a pseudo-photosaturation can occur if there is more than one type of surface states that contributes to the surface band bending (Ref. 153). As discussed in the manuscript, oxygen plays a dominant role in inducing the acceptor-type surface states that are responsible for upward surface band bending in ZnO (also Ref. 152). Therefore, we believe that the surface photovoltage observed here under the photosaturation condition corresponds to the surface barrier height in ZnO nanowires.
C. Supporting Information: Fitting of A1 LO Phonon Frequency ($\omega_{LO}$) as a Function of Temperature

The decrease of the lattice phonon frequency in semiconductors is the result of decreased harmonic frequency due to thermal expansion and anharmonic coupling to other phonon modes. Particularly, taking into account the three-phonon and four-phonon anharmonic interactions, $\omega_{LO}$ can be written as

$$\omega_{LO}(T) = \omega_{LO,0} + \Delta^{(1)}(T) + \Delta^{(2)}(T)$$ (C.1)

with $\Delta^{(1)}(T) = \omega_{LO,0} \{ \exp \left[ -3\gamma \int_0^T \alpha(T')dT' \right] - 1 \}$, (C.2)

and $\Delta^{(2)}(T) = -C \left[ 1 + \sum_{i=1}^{2} \frac{1}{(e^{x_i} - 1)} \right] - D \left[ 1 + \sum_{i=1}^{3} \frac{1}{(e^{y_i} - 1)} + \frac{1}{(e^{y_i} - 1)^2} \right]$ (C.3)

$\omega_{LO,0}$ is the harmonic frequency, $\gamma (=0.74)$ is the Gruneisen parameter of the LO phonon for GaN, $\alpha (= 5.6 \times 10^{-6} /K)$ is the linear thermal expansion coefficient of GaN and is approximated as a constant. $x_i$ and $y_i$ are given by $\hbar \omega_i/k_B T$, with $\sum_{i=1}^{2} x_i = \hbar \omega_{LO,0}$ and $\sum_{i=1}^{3} y_i = \hbar \omega_{LO,0}$. $C$ and $D$ are the three-phonon and four-phonon interaction constants, respectively, with the first (second) term in the expression of $\Delta^{(2)}(T)$ representing the three (four)-phonon anharmonic interactions.

The fitting in Figure 7.2 (c) leads to $\omega_{LO,0} \sim 740$ cm$^{-1}$, with $\omega_1 \sim 636$ cm$^{-1}$, $\omega_2 \sim 104$ cm$^{-1}$ for the three-phonon anharmonic interaction, and with $\omega_1 \sim 580$ cm$^{-1}$, $\omega_2 \sim 97$ cm$^{-1}$, and $\omega_2 \sim 63$ cm$^{-1}$ for the four-phonon anharmonic interaction. $C$ ($\sim 4.11$ cm$^{-1}$) was found to be much larger than $D$ ($\sim 0.06$ cm$^{-1}$), indicating the three-phonon interaction is the dominant phonon anharmonic coupling process. This is consistent with a previous study on an ensemble of GaN nanowires.
Bibliography:


As ZnO nanowires often grow along the [0001] axis ([J. G. Liu, P. Chang, and Z. Fan, Mat. Sci. Eng. R 52, 49, (2006)], the possible Raman scattering geometries corresponding to single nanowires dispersed on substrates is x(yy)x or x(zy)x, with z representing the [0001] direction. With the x(yy)x symmetry, the allowed Raman modes are E2 and A1 (TO) phonons (Ref. 11). In this case, the polarization of the incident laser is perpendicular to the long axis of the nanowire; due to the antenna effects [Q. Xiong, G. Chen, H. R. Gutierrez, and P. C. Eklund, Appl. Phys. A 85, 299 (2006)], the Raman signals would be very weak. We note that a recent observation [(C-T. Chien, M-C. Wu, C-W. Chen, H-H. Yang, J-J. Wu, W-F. Su, C-S. Lin, and Y-F. Chen, Appl. Phys. Lett. 92, 223102 (2008)] of Raman signals from single ZnO nanowires was reported on nanowires with rather large diameters of ~ 200 nm, where weak antenna effects are expected. With the x(zy)x symmetry, while the polarization of the incident laser is parallel to the long axis of the nanowire, the only allowed Raman mode is the E1(TO) phonon, which is characterized by relatively weak scattering cross sections (Ref. 11) and is not observed from the Raman spectrum shown in Fig. 1 (b). In contrast, GaN nanowires usually grow perpendicular to the [0001] direction [e.g. C. Y. Nam, D. Tham, and J. E. Fischer, Appl. Phys. Lett. 85, 5676 (2004)] on silicon substrates. Therefore, for single GaN nanowires dispersed on substrates, LO phonon modes become allowed in the backscattering configuration, as shown in Fig. 1 (c).


84. The integration time for obtaining the high-frequency Raman spectra was 3 minutes. Long exposures to the laser illumination can lead to localized heating. However, the frequencies of ZnO and GaN nanowire lattice phonon modes remained constant under the continuous laser illumination for more than 4 minutes, indicating minimal laser heating effects during the data acquisition process. In addition, we note that, as the 442 nm laser emission is below the bandgap energy of ZnO and GaN, weak absorptions and thus minimal heating effects are expected.


121. See appendix A for current-voltage characteristics of ZnO nanowire Ohmic devices and Schottky diodes, verification of the low-level injection condition, the model of LD as a function of nanowire diameter, and a discussion of obtained S and N.


124. The photocurrent map appears to be "noisier" under forward-biased condition because of a large dark current, which required a lower sensitivity setting of the current amplifier.

125. The localized band bending (or the space-charge region) associated with the Schottky contact can extend into the nanowire region under high reverse biases. However, the photocurrent spatial profile remains unchanged under various biases (not shown here), indicating that the hole transport is diffusion in nature.


127. This value is larger than the nominal NSOM aperture size (100 – 150 nm), probably due to the finite distance between the NSOM probe and nanowire surface;39 the “wear and tear” of the NSOM probe during the scan might also be a factor.


132. If, alternatively, the surface states arise due to the presence of surface adsorbates, a diameter-independent surface electronic structure would lead to a constant S for different
diameters, opposite to our observations. Therefore, the argument of a diameter-dependent surface electronic structure is still valid.


151. We note that, besides the changes in the surface barrier height, the Dember effect, originating from the spatially nonuniform distribution of photogenerated electrons and holes along the laser incident direction (the radial direction in nanowires), can also account for such a SPV. However, the Dember effect requires a high-level optical excitation. Moreover, as the carrier diffusion length (see also the text) is larger than the ZnO nanowire diameter, the radial distribution of photogenerated carriers is expected to be relatively uniform. Therefore, the Dember effect is not expected to play a significant role.


Surface effects are minimized when most of the acceptor-type surface states are neutralized, which is indicated by a large SPV (close to the value of surface barrier height). Close to the metal junction, SPV decreases [Fig. 4 (b)], suggesting that surface effects become
more significant in this region. However, SPV still remains larger than 0.1 V even at the edge of the metal electrode. For the smallest-diameter nanowire, where the surface effects are the strongest, this SPV corresponds to tau around 220 ps, which is larger than the bulk lifetime, indicating that bulk effects are still more significant in limiting the hole transport.


168. The extension of the space-charge region along the nanowire channel can modify the measured surface potential profile close to the metal junction. Additionally, the contributions from KPFM tip-sample interactions can have an impact. However, the space-charge region in ZnO nanowires does not extend into the nanowire channel region at bias lower than 10 V [Hwang, J.-S., Donatini, F., Pernot, J., Thierry, R., Ferret, P., and Dang, L. S., Nanotechnology 2011, 22, 475704]. Also the spatial extension of the KPFM tip point spread function, which describes the tip-sample interactions, was estimated to be ~ 25 nm [Strassburg, E., Boag, A., and Rosenwaks, Y. Rev. Sci. Instrum. 2005, 76, 083705], significantly smaller than LD and within the experimental errors. Furthermore, the SPV profile was obtained by subtracting the surface potential measured in the dark from that measured under the optical excitation; this subtraction is expected to decrease/minimize the contribution of the space-charge region and tip-sample interactions. We note that, under the low-level optical excitation, the dimension of the space-charge region remains unchanged.


197. We note that, since our SThM works in the intermittent contact mode, forced air convection might also be a factor.

199. At the vacuum of 10-6 torr, a residual liquid layer might still be present on the sample surface. However, the intermittent contact mode used here should lead to a decrease in the heat conduction through the liquid bridge. Moreover, the relatively high temperature (~100oC, see also the text) in the nanowire in this case decreases the coverage of liquid film on the nanowire, and thus further diminishes the liquid heat conduction.

200. This is different from what has been suggested in previous studies, where the contribution of the liquid conduction was found to be at least comparable to that of the solid-solid conduction.


204. This model assumes a constant k as a function of temperature. We note that, while the temperature dependence of k in bulk GaN is well known, we are not aware of any reports, experimental or theoretical, for the case of GaN nanowires at high temperatures (higher than the room temperature), the characteristics of which can be significantly different than those in bulk. In Ref. 8, the extrapolation of both experimental and theoretical results on GaN nanowires (with diameters > 90 nm) obtained at low temperatures suggests a relative constant k at high temperatures, at least below 400 K, which is approximately the highest temperature in our nanowire devices (see also the text).


207. Since the laser excitation energy is below the bandgap of GaN, minimal laser heating is expected in these nanowires.

208. While we were only able to measure the temperature using Raman close to the center of the nanowire channel due to the laser heating of the electrodes, if we assume that the SThM signal (delta $V_{th}$) is proportional to the temperature, then we can also estimate the temperatures at electrodes for calculating the average temperature over the entire nanowire channel. We note that, since the temperature is constant over the most of nanowire channel for substrate-supported devices, the contribution from temperature variations in small regions (close to the electrodes) toward $T_{avg}$ is expected to be small.


217. The thermal resistances at the wire-electrode and wire-substrate interfaces also depend on the interface area. Here, for suspended nanowires, from a rough estimate, the length of the wire-substrate interface is \( \leq 1 \mu m \), the area of this interface is comparable or smaller than that of the wire-electrode interface (length \( \sim 1 \mu m \)).

218. Here, we assume that the mechanical bending of the nanowire does not significantly change \( k \). For the device shown in Figures 3(c) and (d), the right electrode is higher than the left one, resulting in different degrees of bending in the two suspended sections. However, the temperature spatial variations in these two sections are relatively similar, supporting, at least to some degree, this assumption.


224. To the best of our knowledge, there are no direct measurements of the minority carrier mobility in ZnO (bulk or nanostructures). However, we observed negligible variances in the majority carrier field-effect mobility measured from ZnO nanowires with different diameters (25 - 60nm). Therefore, we assume that the minority carrier mobility remains constant within the range of diameters studied.

