Steady-state and transient photoconductivity in c-axis GaN nanowires grown by nitrogen-plasma-assisted molecular beam epitaxy

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Analysis of steady-state and transient photoconductivity measurements at room temperature performed on c-axis oriented GaN nanowires yielded estimates of free carrier concentration, drift mobility, surface band bending, and surface capture coefficient for electrons. Samples grown (unintentionally n-type) by nitrogen-plasma-assisted molecular beam epitaxy primarily from two separate growth runs were examined. The results revealed carrier concentration in the range of \((3–6) \times 10^{16}\) cm\(^{-3}\) for one growth run, roughly \(5 \times 10^{14}–1 \times 10^{15}\) cm\(^{-3}\) for the second, and drift mobility in the range of 500–700 cm\(^2\)/(V s) for both. Nanowires were dispersed onto insulating substrates and contacted forming single-wire, two-terminal structures with typical electrode gaps of \(\approx 3–5\) \(\mu\)m. When biased at 1 V bias and illuminated at 360 nm (3.6 mW/cm\(^2\)) the thinner \((\approx 100\) nm diameter) nanowires with the higher background doping showed an abrupt increase in photocurrent from 5 pA (noise level) to 0.1–1 \(\mu\)A. Under the same conditions, thicker (151–320 nm) nanowires showed roughly ten times more photocurrent, with dark currents ranging from 2 nA to 1 \(\mu\)A. With the light blocked, the dark current was restored in a few minutes for the thinner samples and an hour or more for the thicker ones. The samples with lower carrier concentration showed similar trends. Excitation in the 360–550 nm range produced substantially weaker photocurrent with comparable decay rates. Nanowire photoconductivity arises from a reduction in the depletion layer via photogenerated holes drifting to the surface and compensating ionized surface acceptors. Simulations yielded (dark) surface band bending in the vicinity of 0.2–0.3 V and capture coefficient in the range of \(10^{23}–10^{19}\) cm\(^2\). Atomic layer deposition (ALD) was used to conformally deposit \(\approx 10\) nm of Al\(_2\)O\(_3\) on several devices. Photoconductivity, persistent photoconductivity, and subgap photoconductivity of the coated nanowires were increased in all cases. TaN ALD coatings showed a reduced effect compared to the Al\(_2\)O\(_3\) coated samples.


I. INTRODUCTION

Wide-bandgap III-nitride nanowires (NWs) are gaining increased attention for applications involving nanophotonics and nanoelectronics.

1–3 GaN NW structures may be grown by a variety of methods that are now briefly summarized. Laser catalyzed growth has been used to grow [1120] (a-axis) oriented NWs. 1 Core-shell GaN NW heterostructure light-emitting diodes (LEDs) have been realized where catalyst grown a-axis cores were subsequently overgrown with InGaN/AlGaN shells. 2 However, extensive transmission electron microscopy (TEM) analysis on a-axis GaN NWs reveals that they can suffer from a high density of extended defects and basal plane stacking faults. 4 By contrast, [0001] (c-axis) oriented GaN NWs grown by nitrogen-plasma-assisted molecular beam epitaxy (PAMBE) have been shown to be essentially free of strain and defects when examined by x-ray diffraction, TEM, photoluminescence (PL), and nanomechanical studies. 5–9 The characteristically low strain and low defect density of these PAMBE grown c-axis NWs have been observed earlier by other workers (Ref. 10 and references therein), and dense arrays of such structures are being used to realize a new class of GaN LED devices.11,12

An important feature of GaN NWs, given a particular doping level and surface band bending, is that they can be nearly or fully depleted of charge carriers and may conduct in a space-charge limited fashion in certain circumstances. 13 Indeed, it is the control of the depletion layer thickness that enables field effect transistor (FET) sensors based on these structures to function via electrostatic gating by surface adsorbates. 14,15 Control of the depletion layer thickness is also important for the operation of these NW devices as photoductive optical detectors as will become evident within the context of this paper. Back-gated NW FET devices are commonly used to estimate transport properties of the NWs themselves (e.g., carrier concentration and mobility). 3 However, in our experience such approaches for estimating the transport properties of NWs can be unreliable since we find these devices often display gate hysteresis and drift. 16 It is thus desirable to establish alternative approaches for estimating transport properties in NW structures; in this regard, photoconductivity (PC) can offer new insights.
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PC studies of GaN NWs have been reported by a number of authors. Calarco et al.,\textsuperscript{13} described dark conductivity and PC studies as a function of NW diameter for c-axis oriented unintentionally doped (UID) n-type NWs grown by PAMBE. They noted that the surface band bending (in the dark) was approximately 0.55 V for samples thick enough to be undepleted. They observed that the PC mechanism arose from photoexcited holes drifting to the NW surface, screening the depletion field, thereby increasing the diameter of the neutral region and increasing the NW conductivity. It is interesting to note that the basic mechanism of photoexcited holes screening a depletion field to promote gain in planar III-nitride photoconductive detectors has been discussed earlier.\textsuperscript{17}

PC studies of deep levels in metal-organic chemical-vapor deposition (MOCVD) Ni-catalyst grown UID a-axis GaN NWs were performed by Armstrong et al.\textsuperscript{18} where it was observed that majority carrier photoemission from deep levels within the depletion region resulted in increased NW conductivity. PC studies of Si-doped n-type PAMBE grown c-axis NWs were reported by Richter et al.\textsuperscript{19} where they observed that Si incorporation would change the NW growth morphology from essentially uniform in thickness to tapered and conical. They noted that fitting dark current data on a variety of NWs should in principle permit determination of carrier mobility. Mansfield et al.\textsuperscript{20} also reported dark conductivity and PC studies in PAMBE grown Si-doped c-axis GaN NWs, compared the results with back-gated FET behavior on the same samples, and numerical simulations of FET behavior. Moreover, Mansfield et al. estimated the uncertainty involved when attempting to reconcile free carrier concentration, drift mobility, and band bending using dark current and PC data, and also showed that the incorporation of Si in the PAMBE growth process did not appear to substantially alter the NW growth morphology, in contrast to the preceding reference.

II. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

A number of parameters and conventions appearing in this paper are defined as follows: the background n-type donor density is \( N_D \), and it is assumed that such donors are fully ionized, \( n_i \) is the integrated free charge per unit length along a NW, \( n_{ph} \) is the density of photogenerated holes, \( D_i \) is the diameter of a cylinder that inscribes a NW of hexagonal cross section with \( R_i = D_i / 2 \), \( D_m \) and \( R_m \) are the same respective parameters for a circumscribing cylinder, \( D_{av} \) is the diameter of a hypothetical NW of circular cross section with \( R_{av} = D_{av} / 2 \), \( R_r \) is the radius of a cylinder with an equivalent cross sectional area as a hexagon defined by the circumscribing cylinder with radius \( R_r \), the power intensity illuminating a sample at a wavelength \( \lambda \) (in nanometers) is \( P(\lambda) \), the total steady-state current (dark current and photocurrent) under constant illumination is \( I_p \), the initial transient photocurrent at the instant illumination ceases is \( I_p \), the decaying current that persists after illumination ceases is \( I_p(t) \), the maximum “flatband” current conducted in a NW with zero depletion layer thickness is \( I_f \), and the dark current that remains after persistent photocconductivity (PPC) has relaxed is \( I_d \). Other parameters are defined where they appear.

This portion of the paper is organized as follows: Section II A describes NW sample growth and fabrication. Section II B presents an experimental study of steady-state dark current and photocurrent and focuses on samples from growth run B738. Section II C presents a cylindrical depletion model which is applied to samples displaying nonzero dark current. Section II D presents a model describing the time decay of persistent PC. Section II E illustrates the effect on PC that result when NWs are coated with atomic layer deposition (ALD) films. Subbandgap PC is also described in this section.

A. NW growth and processing to fabricate two-terminal photoconductive test structures

The c-axis oriented GaN NWs used in this study were grown by PAMBE on Si(111) substrates. Details on the growth, spectroscopic studies, and mechanical properties of NWs grown in our laboratory are given elsewhere.\textsuperscript{5–9} Notable in these background studies is that the PAMBE grown wires are essentially free of strain and defects. Indeed, TEM reveals that basal plane stacking faults are only found in the interfacial region where the NWs nucleate on the Si substrate and are not found elsewhere in the NWs. Depending on the precise growth conditions, \( D_r \) for the wires examined ranged from roughly 100 to 700 nm. The NWs produced in a particular growth run were generally well formed elongated hexagonal cylinders that were roughly uniform in diameter. The growth rate was in the range from 100 to 300 nm/h and NWs were grown to lengths ranging from 5 to 20 \( \mu \)m.

NWs were ultrasonically stripped off of the Si(111) growth substrates in an isopropanol bath and dispersed with a micropipette onto fused quartz substrates and oxidized Si substrates. Photoconductive test structures were fabricated in two separate formats: (i) wires lying flat on the dispersal substrates and electrically contacted at their ends and (ii) wires electrically contacted at their ends but suspended horizontally above the substrates by a few hundred nanometers, thus forming NW bridge structures. Examples of contacted NWs dispersed flat, and forming a bridge structure, are shown in Figs. 1(a) and 1(b), respectively. The NWs are quite flexible and, as illustrated in Fig. 1(c), in certain instances, a bridging wire would bend down into contact with the substrate without breaking or losing electrical continuity. Various test structures fabricated from NWs taken from the separate PAMBE growth runs are summarized in Table I. For NWs of comparable \( D_r \) taken from a common growth run, there was no significant difference in photoconductive behavior for test structures composed of wires lying flat on dispersal substrates or in the form of bridge structures. The fabrication scheme for NW electrical contacts is now described.

Contacts were formed by electron beam deposition of 20 nm of Ti followed by 200 nm of Al. Subsequent lift-off photolithography yielded a dense array of indexed electrodes with single NWs occasionally bridging an electrode pair. The samples were then processed by rapid thermal annealing.
(RTA) in a flowing atmosphere [1.4 SLM (SLM denotes standard liters/minute)] of 5% H₂/95% Ar. The RTA temperature schedule was ramp from ambient to 100 °C in 5 min, dwell at 100 °C for 5 min, ramp to 500 °C in 10 s, dwell at 500 °C for 60 s, and cool to ambient. The assembly of NW bridge structures employed methods of ac dielectrophoresis\(^2\) to orient the NWs between Ti electrode pads that were photolithographically defined on the substrates. In these experiments, NWs in a solvent suspension were dispersed onto the substrate while an ac voltage was applied between the electrode pads. As the solvent evaporated, the wires would come to rest suspended between adjacent electrode pads, thus forming bridges with the wires elevated a few hundred nanometers above the substrate. Contacts to ends of these bridging NWs were subsequently made using another lithography step and the same Ti/Al metallization and RTA procedure described previously. The electrical conductivity enabled by our metallization and annealing scheme is expected to arise from the diffusion of N from the NW into the Ti layer, thereby producing a TiN layer with a reduced work function compared to the pure metal. Additionally, the N-depleted region in the GaN under the metal contact is expected to have enhanced n-type conductivity via the formation of N vacancies.\(^2\) With this processing scheme, a conservative estimate\(^2\) of the resulting specific contact resistivity is in the range of \((1–10) \times 10^{−5} \ \Omega \ cm^2\). Anticipating the discussion that follows below, we estimated that \(N_d\) is approximately \((3–6) \times 10^{16} \ \text{cm}^{-3}\) for growth batch B738 and approximately \(5 \times 10^{14}–1 \times 10^{15} \ \text{cm}^{-3}\) for batch B992. Following Mohney et al.\(^2\) and assuming an estimated range for drift mobility \(\mu\) of 500–700 \(\text{cm}^2/(\text{V} \cdot \text{s})\), we find that the contact resistance is typically ten times less than the NW resistance considering the typical ranges of NW diameters and electrode gaps given in Table I.

We note that our estimate for \(\mu\) is consistent with the best report (that we are aware of) for MBE grown GaN films. Nikishin et al.\(^2\) reported a Hall mobility of \(800 \pm 100 \ \text{cm}^2/(\text{V} \cdot \text{s})\) for crack-free molecular beam epitaxy (MBE) grown GaN with a n-type background of \((2–3) \times 10^{16} \ \text{cm}^{-3}\). Using a conservative estimate for the Hall factor of roughly 1.2–1.3 for GaN,\(^2\) our presumed range in drift mobility \(\mu\) is reasonable and is also consistent with the estimated results that follow below. Taken together, these observations and estimates lead us to conclude that most of the voltage is dropped across the NW, and the resistance of the contacts may be ignored in the subsequent analysis.

![FIG. 1. (a) Single NW lying flat on a fused quartz substrate and electrically contacted at the two ends. This image corresponds to sample 7, as enumerated in Table I. (b) Example of a NW bridge structure. The sample rests roughly 200 nm above the surface of the fused quartz substrate. (c) NW flexibility is illustrated in this image. During dielectrophoresis alignment, the portion of the NW between the pads sagged and adhered to the substrate via van der Waals forces. Despite appearance to the contrary, this device was unbroken and exhibited electrical continuity.](image)

<table>
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<th>Sample</th>
<th>(D_x) (nm)</th>
<th>(L_x) ((\mu m))</th>
<th>(I_{\text{f}})</th>
<th>(I_p)</th>
<th>(V_a) (V)</th>
<th>(I_{\text{ALD}}) (A, T)</th>
<th>Batch/die</th>
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<td>5.4 (\mu A)</td>
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B. Dark current and steady-state photocurrent in GaN NWs

The NW test structures were examined with a computer-automated current-voltage (I-V) probe apparatus that permitted simultaneous illumination in the visible-UV band while the I-V characteristics were being scanned and recorded. All measurements were performed at room temperature in ambient air. A schematic of the apparatus is illustrated in Fig. 2. The light source was a 75 W Xe arc lamp dispersed by a 150 mm focal length monochromator that operated with a spectral bandwidth of roughly 5 nm. The monochromator output was focused using fused silica optics to a maximum illumination intensity of 105 W/cm2 at 360 nm for near/above-bandgap excitation of a sample under test. Higher UV intensities were provided by a HeCd laser operating at 325 nm which provided a maximum illumination intensity $I_{325}$ =475 W cm$^{-2}$ with the optics available.

Starting first with a discussion of the thicker NWs that displayed nonzero dark current (Table I, samples 1–5, growth run B738), examples of the dark and steady-state PC behavior are now presented. A field emission scanning electron microscopy (FESEM) image of sample 1 is given in Fig. 3(a) and $I_p$-V (dark) and $I_{ph}$-V [maximum $P_{360}$ (360 nm illumination)] data for this sample are illustrated in Fig. 3(b). Graphs of $I_p$ as a function of $P_{360}$ and $P_{325}$ for samples 3 and 5 are given in Figs. 3(c) and 3(d), respectively. The power intensity was varied by means of neutral density filters and the bias was 0.1 V in both cases. The bias was chosen to keep the maximum $I_p$ from exceeding a few microamperes since devices would often fail at higher currents. The data illustrated in Fig. 3(c) indicate that $I_p$ rises steeply with increasing illumination intensity until $P_{325}$ $\approx$ 10 W cm$^{-2}$, but rises with significantly reduced slope thereafter. This effect is interpreted as a screening of the depletion field by photogenerated carriers.

The NW geometry offers a confinement structure that allows one to equate time resolved photoluminescence (TRPL) lifetime to minority carrier lifetime $\tau$, as described by Ahrenkiel.\textsuperscript{28}

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$P_{325}$ $\approx$ 100 W/cm$^2$, $n_{ph}$ becomes large enough to substantially screen the depletion field and allow the neutral conducting region to expand resulting in increased NW conductivity. This approximate analysis also reveals that the surface density of photogenerated holes available to screen the depletion field is $\approx$2 $\times$ 10$^{11}$ cm$^{-2}$ at this illumination intensity. As discussed in more detail below, for the samples considered in this study, a photogenerated surface hole density in the range of $(2\sim8)\times$10$^{11}$ cm$^{-2}$ should fully screen the depletion field so that $I_p$ $\approx$ $I_f$. However, a photoexcited hole density of roughly $2\times$10$^{10}$ cm$^{-2}$ should partially screen the depletion field such that $I_p$ may fall within 90%–95% of $I_f$. Hence, we interpret the inflection illustrated in Fig. 3(c) where $P_{325}$ $\approx$1–10 W/cm$^2$ as a transitional regime whereby for $P_{325}$ $<$ 1 W/cm$^2$, PC is dominated by partial screening of the depletion field by photogenerated holes while for $P_{325} > 10$ W/cm$^2$, the structure behaves more as a conventional photoconductor\textsuperscript{30} in the sense that the density of photogenerated electrons becomes comparable or exceeds $N_d$ with increasing $P_{325}$. Similar behavior is seen for sample 5, as illustrated in Fig. 3(d), although this sample displays comparatively low dark current and is nearly depleted in the dark.

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The representative behavior of the thinner NWs (depleted in the dark) from batch B738 is illustrated in Fig. 4(a) for sample 7. This figure illustrates $I_f$-V data for various constant values of $P_{360}$. Figure 4(b) illustrates $I_p$ for this sample under a constant bias of 0.8 V as a function of vary-
ing levels of $P(360)$ and $P(325)$ up to a maximum of roughly $P(325) = 10 \text{ W cm}^{-2}$. Experimental limitations precluded illuminating this sample at the maximum value of $P(325) = 475 \text{ W cm}^{-2}$ as described for samples 3 and 5. Sample 6 is an example of a bridge structure formed from a thinner NW. A FESEM image of this sample is shown in Fig. 5(a). The $I-V$ characteristics under UV illumination and in the dark are shown in Fig. 5(b). The results illustrating the behavior of samples 6 and 7 are generally observed for the thinner NWs (whether they are bridge structures or lying flat on substrates), e.g., $I_p/I_d = 10^{4-10^5}$. Comparable photoconductive behavior in MBE grown $c$-axis GaN NWs depleted in the dark was also given by Calarco et al.\textsuperscript{13}

The logarithmic scale used to display the magnitude of $I_p$ in Figs. 4(a) and 5(b) partially obscures the fact that the $I_p-V$ plots for the thinner NWs of this batch (samples 6–8) are sometimes asymmetric and not perfectly linear, whereas both the $I_p-V$ and $I_d-V$ behaviors of the thicker samples (samples 1–5) are usually perfectly linear. Precedent for this trend is also seen in the results of Ref. 13 for PAMBE grown GaN NWs that apparently contain a $n$-type background carrier concentration that is comparable to what we observe. We argue that this behavior is not unexpected in the thinner samples for the following reasons. Given the contact fabrication scheme, the portion of the NW beneath and in the immediate vicinity of the metal contact should be quite conductive as previously discussed. On the other hand, the portion of the wire extending away from the metal contact is fully depleted in the dark and partially depleted under UV excitation. Hence, a band offset should exist between the more highly conductive GaN directly beneath the metal contact and the axially adjacent portion of the NW protruding away from the contact. Variations in contact processing conditions, slight tapering of the wires, etc., would lead to unequal barriers at either end of the NW. We speculate that the apparent partial Schottky-like behavior observed for some of the thinner NWs under UV illumination and the variation in $I-V$ asymmetry with UV illumination intensity as seen in Figs. 4(a) and 5(b) may arise from these effects.

C. Analysis of steady-state dark current and photocurrent in GaN NWs

1. Cylindrical model to simulate depletion in NWs of hexagonal cross section

As illustrated in Fig. 6, we assume that the NW may be approximated by a cylinder of diameter $D_m$ with uniform $n$-type doping density $N_d$ leading to a free carrier concentration of the same density. The NW is partially or fully depleted by the presence of surface acceptor states of density $N_a$ resulting in an undepleted conducting neutral region of radius $r_o$ within the wire. The maximum upward bending of the conduction band between the undepleted neutral region of the NW and the fully depleted surface is defined as $\phi_m$. This convention should be distinguished from the surface potential $\Phi_s$ defined by $\Phi_s = E_F - E_F$ in a manner consistent with the usage of other authors.\textsuperscript{13,13f} An approximate expression for $\phi_m$ is derived by assuming an abrupt depletion boundary and using Gauss’ law and the cylindrical symmetry to first calculate the radial electric field in the space-charge region and then computing $q\phi_m$, the work required to move a test charge from $r_o$ to $R_m$. This simple temperature independent analysis gives

$$\phi_m = \frac{qN_d}{2\varepsilon} \left[ \frac{R_m^2 - r_o^2}{2} - r_o \ln \left( \frac{R_m}{r_o} \right) \right].$$

(1)

In the preceding equation, $q = 1.602 \times 10^{-19}$ C and $\varepsilon = \varepsilon_r\varepsilon_r$, where $\varepsilon_r = 8.54 \times 10^{-14}$ F/cm and $\varepsilon_r = 8.9$. 

FIG. 4. (a) $I_p-V$ for sample 7 at a wavelength of 360 nm taken at various values of illumination intensity. The magnitude of the current is plotted for negative voltage swings. A: 0.65 $\mu$W cm$^{-2}$; B: 4.3 $\mu$W cm$^{-2}$; C: 41.0 $\mu$W cm$^{-2}$; D: 0.35 mW cm$^{-2}$; and E: 3.6 mW cm$^{-2}$. (b) $I_p-P(360)$ and $I_p-P(325)$ for sample 7 under a constant applied bias of 0.8 V. Experimental limitations prevented attaining the maximum value for $P(325) = 475 \text{ W cm}^{-2}$ that was illustrated in Figs. 3(c) and 3(d).

FIG. 5. (a) FESEM image of NW bridge (sample 6). The bridging NW is partially obscured by an adjacent non-bridging NW as indicated. (b) $I_p-V$ and $I_d-V$ for sample 6. UV illumination: 3.6 mW cm$^{-2}$ at 360 nm.

FIG. 6. Schematic of conduction and valence band bending for partially depleted cylindrical NW in the dark at equilibrium. The diameter $D_m = 2r_o$. The $n$-type NW contains a fully ionized donor density $N_d$. The surface supports a density $N_a$ of ionized acceptors that trap conduction electrons, resulting in a cylindrically symmetric depletion region and upward bending bands. The Fermi level is “pinned” near midgap at the surface, as shown. The neutral region of the NW of diameter $2r_o$ that will conduct electrical current is indicated. The insulating depletion region supports the upward band bending shown. The maximum band bending of the conduction band between the undepleted region and the NW surface is defined as $\phi_m$. The surface potential is defined by $\Phi_s = E_F - E_F$ evaluated at the surface, as shown.
We mention that Eq. (1) is a special case of the more general (but still approximate) cylindrical analysis given by Dobrokhotov et al. in their work on GaN NW gas sensors functionalized with metal nanoparticles. An example solution of Eq. (1) as a function of \( r \) is given in Fig. 7, where representative values \( N_d = 7 \times 10^{16} \text{ cm}^{-3} \) and \( R_m = 150 \text{ nm} \) are used. Figure 7 also illustrates that the band bending becomes approximately parabolic as the depletion layer becomes thin compared with the NW diameter as expected from the standard planar depletion model.

The upward bending of the conduction band for GaN surfaces has been estimated by electron photoemission, scanning Kelvin probe microscopy, and theoretical work. From the results of those studies we expect that \( \phi_m \) should fall somewhere in the range of roughly 0.1–1.1 eV. Additionally, Ref. 33 reports that there should be no significant difference in surface band bending between polar \( c \)-plane surfaces and nonpolar \( a \)-plane surfaces for MOCVD grown GaN films. Notably, the band bending for GaN can be strongly influenced by surface treatments and Ga/N flux ratio in the case of MBE growth. This latter point is significant for the present discussion since the PAMBE process that enables the NW growth morphology requires a much higher N to Ga flux ratio than what is typically used for conventional MBE growth of GaN films.

Given this range of estimates reported in the literature, there is no a priori reason to presume that \( \phi_m \) for our samples that are examined in ambient air should be as high as 1.1 V, as reported in Ref. 33, or necessarily \( \approx 0.55 \text{ V} \), as reported for the \( c \)-axis PAMBE grown GaN NWs in Ref. 13 since the latter are not grown under exactly the same conditions as ours.

Given its convenience and simplicity, one is particularly interested in the validity of Eq. (1) as \( \phi_m \approx -kT/q \), and how well the cylindrical representation of the hexagonal NW cross section applies in this limit. We examined these issues as follows: A temperature dependent numerical Poisson solver applied to a NW geometry of hexagonal cross section was used to compute \( n_L \) (the integrated free charge per unit length of a NW) for the representative cases including \( \phi_m = 0.2, 0.4, 0.6, 0.8 \text{ V} \); \( N_d = 4 \times 10^{16}, 8 \times 10^{16}, \) and \( 1.2 \times 10^{17} \text{ cm}^{-3} \); and \( D_i = 220, 280, 320 \text{ nm} \). In these simulations, the acceptor density \( N_d \) was taken as uniform over the NW surface and its value was adjusted to compute the values of \( \phi_m \) just listed (at the tangential points where \( D_i \) intersects the hexagonal faces). The computed span of \( N_d \) ranged from \( 2 \times 10^{11} \text{ cm}^{-2} \) (smallest \( D_i \), \( N_d \), and \( \phi_m \)) up to \( 8 \times 10^{11} \text{ cm}^{-2} \) (largest \( D_i \), \( N_d \), and \( \phi_m \)). Moreover, given the estimates of minority carrier lifetime and absorption coefficient previously discussed in the context of Figs. 3(c) and 3(d) we conclude that \( P(325) \) in the range of \( 10^2–10^3 \text{ W/cm}^2 \) should be sufficient to nearly or fully screen the depletion field over these representative spans of \( D_i \), \( N_d \), and \( \phi_m \). The simulation also reveals that \( \phi_m \) is a strongly nonlinear function of \( N_d \) and for \( N_d \approx 2 \times 10^{10} \text{ cm}^{-2} \), the integrated free charge per unit length \( n_L \) is within 90%–95% of the flatband value. Thus we expect that a density of photoexcited holes \( n_{ph} \) of roughly \( 2 \times 10^{10} \text{ cm}^{-2} \) will yield \( I_p = I_d \).

The span of values of \( \phi_m \) and \( N_d \) listed in the previous paragraph was then used as input to calculate \( n_L \) by means of Eq. (1). In these calculations \( R_m \) was varied until the computed values of \( n_L \), equated with those obtained using the Poisson solver for the examples of \( D_i \) listed. \( D_m \), calculated in this fashion represents the diameter of an “equivalent” cylindrical NW and we label this diameter as \( D'_m \). We thus arrived at the values for \( D_m \) of \( D'_m = D_i + 13 \pm 5 \text{ nm} \), \( D_i + 10 \pm 3 \text{ nm} \), and \( D_i + 9 \pm 4 \text{ nm} \) that correspond, respectively, to the three cases of \( N_d \) just listed. Hence, over this representative span of \( \phi_m \), \( N_d \), and \( D_i \), we find that \( D'_m - D_i \approx 10 \text{ nm} \). It is also instructive to compare the thickness of the depletion layer derived in the foregoing analysis to the effective Debye length \( L_d \), where \( L_d = \sqrt{\epsilon k T q^2 N_d} \) (assuming that only donors are present). Then another statement of the applicability range of Eq. (1) is that the depletion layer thickness \( D'_m / 2 - r_0 \) should be greater than roughly four to five effective Debye lengths. Hence, the depletion in a NW of hexagonal cross section for the diameters considered can be reasonably represented by a cylinder of constant diameter \( D'_m \) (with \( D'_m = D_i + 10 \text{ nm} \)), and Eq. (1) is an approximate representation of the depletion in this structure provided that 0.2 V \( \leq \phi_m \leq 0.8 \text{ V} \) and \( 4 \times 10^{16} \text{ cm}^{-3} \leq N_d \leq 1.2 \times 10^{17} \text{ cm}^{-3} \).

2. Graphical analysis of steady-state dark current and illustration of uncertainties

The numerical problem for analyzing the steady-state dark conductivity in the NWs involves first examining samples with measurable dark current \( I_d \) and then calculating estimates of \( N_d \), \( \mu \), and \( \phi_m \) from

\[
I_d = N_d \mu q \pi r_0^2 V_a / L_s,
\]

where \( L_s \) is the electrode gap and \( V_a \) is the applied voltage. Under the assumption that NWs from a common growth batch have common transport properties and surface band bending, one might expect that measurements of \( I_d \) from at least three separate NWs could allow for the unique determination of \( N_d \), \( \mu \), and \( \phi_m \). In practice, however, this is not
feasible since the uncertainty in the measurements of the NW diameters is a significant limitation in this analysis as we now illustrate.

Consider three hypothetical two-terminal cylindrical NW structures with respective diameters $D_m^{1,2,3}$ = 250, 300, and 380 nm. We set $\phi_m = 0.6$ V, $N_d = 1 \times 10^{17}$ cm$^{-3}$, $\mu$ = 300 cm$^2$/V s, $L_g = 4$ $\mu$m, and $V_a = 1$ V for each NW. Equations (1) and (2) may be used to numerically solve for the respective dark currents conducted in these wires, yielding $I_d^{1,2,3}$ = 0.3868, 1.4655, and 4.226 $\mu$A. Figure 8(a) illustrates the locus of solutions of Eq. (2) for $N_d$ and $\mu$ corresponding to the input values of $I_d^{1,2,3}$ and the simultaneous solution conforming to the initially assigned values of $N_d$ and $\mu$. Also illustrated in the figure is the computed flatband condition where $\phi_m = 0$ and $r_c = R_m$ for each NW, yielding solutions that are necessarily degenerate for the three cases. In Fig. 8(b) we use $\phi_m = 0.7$ V and illustrate the locus of permissible solutions for $N_d$ and $\mu$ when an uncertainty in diameter $\delta D_m = \pm 10$ nm for each NW is included. This results in a range of possible simultaneous solutions of equal probability with $N_d$ spanning roughly from 0.94 to 1.12 $\times 10^{17}$ cm$^{-3}$ and $\mu$ spanning roughly from 225 to 425 cm$^2$/V s. The possible solutions for $N_d$ and $\mu$ also depend strongly on $\phi_m$, as illustrated in Fig. 8(c), where we show an additional example resulting from $\phi_m = 0.3$ V. Thus, under the assumption that the cylindrical representation of a NW is accurate, the “correct” values for carrier concentration and mobility, i.e., $N_d = 1 \times 10^{17}$ cm$^{-3}$ and $\mu$ = 300 cm$^2$/V s, cannot be recovered without significant error even when the $\delta D_m$ is only a few percent of the NW diameter. We now apply these graphical methods to estimate ranges of $N_d$ and $\mu$ for samples described in Table I that displays nonzero dark current, and then check the consistency of the results with the observed photocurrent.

In Fig. 9 we illustrate the result for samples 1–4 where a representative span in $\phi_m$ from 0.2 to 0.6 V is considered. Table I gives the corresponding values of $I_d$, $V_a$, $L_g$, and $D_m$ used as input for each sample in the calculation. We consider the maximum uncertainty in diameter by calculating results using estimated minimum and maximum values of diameter for each sample. The extrema in $D_m$ are estimated as follows: FESEM was used to measure $D_m$ in plan view. The NWs typically rest with a hexagonal facet in contact with the substrate (or bottom electrode pad). Thus, $D_m \approx D_c$, and values of $D_c$ appearing in Table I correspond to such estimated maxima. The estimated minimum NW diameters $D_i$ correspond to inscribed cylinders as defined earlier. As shown in Fig. 9, when this estimated maximum uncertainty in the NW diameter is taken into account, the measured values of $I_d$ for growth batch B738 can be accommodated over the given representative range of $\phi_m$ with $\mu$ spanning from roughly 100 to 750 cm$^2$/V s and the corresponding range of $N_d$ spanning from $1.8 \times 10^{17}$ down to $4.0 \times 10^{16}$ cm$^{-3}$. Note that Table I also includes sample 5 that exhibits the lowest nonzero $I_d$ of batch B738. However, since this sample is relatively close to depletion, it is poorly simulated by Eq. (1) and its measured value of $I_d$ does not map onto Fig. 9 using the procedure just described. The samples of batch B992 cannot be analyzed by this procedure since there is only sample 9 thick enough ($D_c = 680$ nm) to permit nonzero $I_d$. The experimental results obtained from batch B992 suggest that $N_d$ for this batch should be roughly ten times less than for the B738 sample set. This point will be discussed further in Sec. II E.
D. Analysis and simulation of persistent photocurrent decay

1. Development of model

An approximate model for the time decay of the persistent photocurrent $I_p(t)$ is now developed. Our approach is motivated by the work of Reshchikov et al. in their study of UV-induced transient photovoltage in planar GaN films. Under uniform above-bandgap illumination, photogenerated holes are swept to the NW surface by the depletion field and trapped. This accumulation of holes on the surface effectively compensates the negatively charged surface acceptors and reduces the upward bending of the conduction band to $\Phi_L$, where $\Phi_L < \phi_m$. The NW becomes less depleted, and the radius of the neutral region increases to $r_L$ with $r_L < r_D$. This nonequilibrium situation is depicted in Fig. 10(a).

When the illumination is ceased, an instantaneous initial persistent current $I_p^0$ flows and the total initial current in the NW is $I_p^0 + I_d$. Recombination occurs via electrons at the bottom of the conduction band in the neutral region surmounting the surface barrier $\Phi_L$ by thermionic emission and recombining with trapped holes at the surface. As the process continues, $\Phi(t)$ eventually returns to the dark equilibrium value $\phi_m$.

Capture coefficient, and the density of thermally activated electrons from the bottom of the conduction band in the neutral region of the NW that is available for surface recombination is given by $N_d$ multiplied by the Boltzmann factor. $C_n$ is related to the capture cross section $\sigma_t$ by the relation $C_n = \sigma_t \sqrt{kT/\pi m_n}$, where $m_n$ is the effective mass of conduction band electrons and $m_n = 0.20 m_e$, yielding $C_n = \sigma_t 2.4 \times 10^7$ cm$^{-2}$.37

Equation (3) is readily put into a form amenable to numerical simulation with the following arguments. From the requirement of charge neutrality between the surface and the depletion region, the steady-state density of ionized surface acceptors in the dark may be expressed as $N_d = (N_d/2R_m) \times (R_m^2 - r_D^2)$. Similarly, the steady-state population of ionized surface acceptors under constant illumination is $N_d^1 = (N_d/2R_m) \times (R_m^2 - r_D^2)$. Thus, the steady-state population of photexcited holes under constant illumination is $p^1 = N_d^1 - N_d^2$. When the illumination ceases, the time dependent population of photexcited holes is then $p(t) = N_d^2 - N_d(t)$. The time dependent undepleted cross sectional area of the NW arising from photoexcitation is defined as $A(t)$, where $A(t) = \pi (r_D^2 - r_D^2)$. Thus $p(t) = N_d A(t) / (2 \pi R_m)$ and Eq. (3) is recast as

$$\frac{dA(t)}{dt} = -A(t)C_n N_d \exp \left(-\frac{\Phi(t)}{kT}\right).$$  (4)

The time dependence of the surface band bending $\Phi(t)$ is obtained from Eq. (1) with $r_o$ replaced by $\sqrt{r_D^2 + A(t)/\pi}$. Clearly $I_p(t) = N_d \mu A(t) V_c / L_c$, so that the solution of Eq. (4) is proportional to the time decay of the persistent photocurrent. Equation (4) is solved numerically using an adaptive step fourth-order Runge–Kutta algorithm. The specific Runge–Kutta coefficients are used by Carnahan et al.38

To put this into context, we compute example solutions of Eq. (4) representing the time decay of normalized persistent photocurrent for an undepleted NW where $N_d$, $\phi_m$, and $\sigma_t$ conform to values of these parameters used in the analysis of transient photovoltage for planar GaN films presented in Ref. 37. These results are illustrated in Fig. 11(a) where $D_m = 200$ nm, $N_d = 3 \times 10^{17}$ cm$^{-3}$, $\phi_m = 0.65$ V, and three values for capture cross section $\sigma_t$ are used ($10^{-16}$, $10^{-15}$, and $10^{-14}$ cm$^2$). The model is not expected to apply when $R_m$...
- $r_o(t) < 4 - 5L$; thus, we calculate that the initial condition at which Eq. (4) should reasonably represent the decay of normalized photocurrent $\bar{I}(t)$ in this example starts at the point where $\bar{I}(t=0) = 0.45$ and $[r_o(t)/R_m]^2 = [I_p(t)+I_d]/I_f = \bar{I}(t)$. Both our model and that of Ref. 37 can be viewed as similar; however, there are some clear distinctions. Within the constraints previously discussed, our model solves for the full time dependent evolution of the surface band bending for a GaN cylinder and the corresponding time dependent cross sectional area of the neutral region. By contrast, Ref. 37 finds the time evolution for the surface band bending for a planar GaN film within the approximation that the photoinduced variation in band bending is small compared to the dark surface band bending. Hence, one would expect similar, but not directly comparable results for the same input values of $N_d$ and $\sigma_n$ applied to both situations. In particular, in Fig. 11(a) we find that the persistent photocurrent should decay in roughly 50–100 s when $\sigma_n = 10^{-15}$ cm$^2$ which is qualitatively consistent with the temporal evolution of surface band bending, as calculated in Ref. 37. As a second example, Fig. 11(b) illustrates the case for $D_m$ = 350 nm, $N_d$ = $5 \times 10^{16}$ cm$^{-3}$, and $\phi_m$ = 0.3 V, and $\sigma_n$ in the range from $10^{-22}$ to $10^{-20}$ cm$^2$ are used. The starting time of the simulation was adjusted to account for constraint imposed by $L$ as previously described. Of course our key task is to consider the inverse problem, i.e., fitting the simulation to the photocurrent decay data in an effort to solve for $N_d$ and $\sigma_n$. The ideal uniqueness of these fitted solutions is discussed in the Appendix.

Fitting the temporal decay of the persistent photocurrent for wires with nonzero $I_d$ offers a means to further restrict the estimated acceptable ranges of $N_d$ and $\mu$ as follows. For a given NW with measured $I_p$, $I_p^0$, $I_d(t)$, and $D_c$, the ratio of dark current to flatband current is given by $I_p/I_d = (r_p/R_p)^2$. From the earlier estimates of the range of $n_p$ is necessary to attain 90%–95% of flatband conditions, and using Figs. 3(c) and 3(d), $I_f$ falls into the approximate range of $2.5I_p^0 < I_f < 5I_p^0$. The resulting span of $I_p/I_f$ is then 0.2–0.4, and we may compute the corresponding bounds on $r_p(t)$ given $I_d$ and $D_c$. Using these quantities and $D_{mn}$ we vary $N_d$ and $\sigma_n$ in a least-squares minimization procedure to fit Eq. (4) to $\bar{I}(t)$ for the case at hand.

2. Analysis of samples from batch B738

Figures 12(a)–12(d) illustrate fitting the decay of $\bar{I}(t)$ for samples 1 and 2. Here the data were normalized and the start times $t_o$ for the simulations were constrained as previously described. The start time of the simulation shown in Fig. 12(a) for sample 1 (the thickest samples from batch B738) occurred at $t_o = 0$ (at the start of the actual photocductive decay) under the assumption that $\bar{I}(t=0) = 0.2$. In Fig. 12(b), however, the fit of the same data was performed for $\bar{I}(t=0) = 0.4$ and $t_o$ was necessarily delayed until $\Phi(t)$ had recovered sufficiently such that the cylindrical depletion model was valid. Figures 12(c) and 12(d) show similar fitting of $\bar{I}(t)$ data for sample 2. Analysis of samples 3 and 4 gives similar results but utilizes less of the available data since $t_o$ must be delayed further in order to accommodate the limitations of the depletion approximation imposed by these progressively thinner samples. Sample 5 is too thin to apply the model even though its $I_d \neq 0$.

The simulations reveal that the estimated uncertainty in setting the normalization of $I_k(t)$ results in the fitted solutions for $N_d$ and $\sigma_n$ spanning roughly $(3–6) \times 10^{16}$ cm$^{-3}$ and $10^{-23}$–$10^{-19}$ cm$^2$, respectively. These results for $N_d$ taken together with the (dark) current-voltage data presented in Fig. 9 suggest that $\mu$ should fall in the range of roughly 500–700 cm$^2$/V s. This result is consistent with our prior assertion that $\mu$ for UID MBE grown GaN NWs should be comparable to $\mu$ extrapolated from Hall mobility data reported for crack-free MBE GaN films with comparable $n$-type background that was grown on Si(111).26

The fully depleted NWs from this batch (samples 6–8 with $D_c$ spanning 105–113 nm) typically showed faster photocductive decay [as illustrated in Fig. 13(b), sample 8, for the case of no ALD coating]; however, these samples are too thin to permit fitting the simulation to the data using the foregoing procedure. The $I_d$ versus $P(360)$ data illustrated in Fig. 4(b) for sample 7 is generally representative of these depleted NWs from this batch and we again expect that $I_d$ is within 90%–95% of $I_f$ for $P(325) = 10$ W/cm$^2$ and that $0.2I_f < I_p < 0.3I_f$ for $P(360) = 3.6$ W/cm$^2$.

According to Ref. 37, our estimated range of $\sigma_n$ ($10^{-19}$–$10^{-23}$ cm$^2$) should be comparatively low for semi-
E. Effects of ALD coating on NW conductivity and examples of below-gap PC behavior

Figures 13(a) and 13(b) illustrate the comparative photoconductive behavior under illumination at 360, 380, 400, and 550 nm for samples 1 and 8 before and after these devices were conformally coated with roughly 10 nm of Al2O3 by ALD. ALD coating was performed using trimethylaluminum and H2O as the reactants.41-43 There are significant distinctions to note in comparing PC and PPC before and after ALD coating. For example, prior to Al2O3 coating, we generally found relatively weak subgap PC which would become more prominent after ALD coating. Additionally, the decay rate of the persistent current for a given device prior to coating was comparable for all illumination wavelengths that yielded PC, even though, as seen in Figs. 13(a) and 13(b), there was a considerably reduced photoresponse for the excitation wavelengths greater than 360 nm. However, after Al2O3 coating, the photoconductive response at all excitation wavelengths and the decay time were substantially increased.

An example of the long-term aging behavior of PPC for sample 6 coated with Al2O3 is illustrated in Fig. 14. Prior to ALD coating, this sample showed no measurable photocurrent under ambient light illumination. The photoconductive decay time for this sample prior to ALD coating was comparable to that displayed by sample 8 in Fig. 13(b). UV PC experiments were performed on sample 6 roughly 1 month after the ALD coating. It was then stored for 17 months in ambient light conditions. Figure 14 illustrates the UV photoresponse and PPC decay recorded within 1 month of ALD coating and the photoconductive behavior taken after 17 months. The latter starts with the photocurrent recorded under ambient light, as shown, followed by exposure to UV light. When the UV light was switched off, the PPC decay in the dark was initially much faster than that illustrated in the initial experiment. However, the photocurrent measured under ambient light conditions is not recovered after 7 days of monitoring Ipc(t) in the dark. Figures 15(a) and 15(b) illustrate comparative PPC under 360 nm exposure before and after ALD Al2O3 coating of samples 9 and 10 from growth batch B992; they show that the Al2O3 coatings produce a comparable change in behavior of photoconductive response for NWs from both growth runs.

Table I tabulates data for Ipc [photocurrent for P(360) = 3.6 W/cm² before ALD coating] with Ipc,ALD [photocurrent for P(360) = 3.6 W/cm² after ALD coating] for samples from batch B738. Combining these results with the previous estimates of Ipc for these samples reveals that the effect of ALD Al2O3 coating increases the photocurrent such that Ipc,ALD ∝ Ipc for P(360) = 3.6 W/cm². ALD Al2O3 has been reported to introduce interface trap states for GaN whose density depends on processing and annealing conditions.44 Our results showing increased conductivity and a slowing of the
decay rate of PPC in the Al₂O₃-coated NW devices suggest that the oxide layer introduces long-lived hole traps such that the surface band bending is substantially reduced under UV illumination and recovers far more slowly (if at all) in the dark compared to the uncoated cases. By contrast, studies of comparative PPC on GaN NWs under vacuum and exposed to air suggest that adsorbed oxygen plays a role in accelerating PPC decay.⁴⁵

We generally observe consistent conductivity and PC behavior for NWs taken from a single growth run but differences in behavior between growth runs. On the other hand, the low strain and defect-free nature of the NWs is maintained from run to run. Such trends were evident for the two UID n-type sample batches considered in this paper and for the study of Si-doped n-type NWs published separately.⁴⁰ We would expect differences in UID n-type behavior between sample batches because it is difficult to duplicate exactly the same PAMBE growth conditions between growth runs. Furthermore, one would expect that such differences would become more evident for samples with relatively low background carrier concentration. Drawing from our earlier arguments based on the high structural quality of these NWs, μ for batch B992 should also be in the range of 500–700 cm²/(V s). Furthermore, when these wires were ALD coated with Al₂O₃ we would also expect that \( I_{\text{ALD}} = I_f \) for \( P(360) = 3.6 \text{ W/cm}^2 \). Taken together, these estimates are consistent with \( N_d = 5 \times 10^{14} - 1 \times 10^{15} \) for this wire batch.

Other ALD coating schemes were also explored on both sample batches. We performed comparative 360 nm PPC experiments on NW devices (samples 11 and 13–16) before and after they were coated with roughly 7 nm of TaN by ALD. The coating was performed using (tert-butylidylo)tris(diethylamido) tantalum and hydrazine as the reactants.⁴⁶ The results are summarized in Table I. Figures 16(a) and 16(b) illustrate the respective results of PPC decay for samples 15 and 16. Since the intent of these TaN coating experiments was to obtain a qualitative comparison with the Al₂O₃ ALD-coated samples, we did not take extra steps to ensure that all test structures supported only a single NW between the electrodes. Figure 16(a) shows the PPC behavior for sample 15 consisting of two NWs from batch B738 (with approximate diameters of 76 and 160 nm) that bridged a common electrode gap of 3.4 μm with –1 V dc bias applied. The observed photocurrent prior to ALD coating was consistent with only the thinner wire conducting under UV illumination. The TaN ALD-coated sample shows increased PPC compared to the bare sample, but the effect is far less than that illustrated in Fig. 13(b) for Al₂O₃-ALD-coated samples of comparable diameter from the same growth batch. Figure 16(b) illustrates the results for sample 16 consisting of two bridging wires (with approximate diameters of 150 and 200 nm) taken from batch B992, where the electrode gap was 4.5 μm and +1 V dc bias was applied. In this case we found that the effect on the PPC of the TaN ALD coating was essentially negligible. As noted in Table I, samples 11, 13, and 14 all showed an increase in peak PC after ALD TaN coating, but we did not observe any significant change in the PPC decay time compared to that for the uncoated state of these samples.

Finally, we remark that control experiments were performed to check for possible conductivity and PC in both the Al₂O₃ ALD and TaN ALD films. In these experiments, the electrical continuity before and after ALD coating was checked between contact pads that were devoid of any connecting NWs. In no case was conductivity or PC of the ALD deposited films resolved within the sensitivity of our measurements.

III. DISCUSSION

Measurement of transport properties in semiconductor NWs often involves the fabrication of FET devices and esti-
mation of carrier concentration and mobility from the conductance and pinch-off conditions. Some authors have cautioned that the results of such analyses will depend strongly on the sophistication of the simulation tools and the model employed. Our own observations of drift and hysteresis in NW FET devices further illustrate that the application of sophisticated simulation tools does not necessarily guarantee reliable extraction of transport properties. The methods presented herein offer an alternative approach for estimating $N_d$, $\mu$, and $\phi_m$ and require the fabrication of relatively simple two-terminal NW devices rather than three-terminal FET structures. The combination of the $I$-$V$ and time decay measurements offers a useful “cross-check” since the latter do not depend on mobility. However, for the dark $I$-$V$ measurements, one must employ a range of NW diameters such that the set of samples spans from fully depleted in the dark to substantially undepleted while at the same time conforming to the limitations in the depletion approximation as described earlier. Of course, abandoning the convenience and simplicity offered by the cylindrical depletion model of Eq. (1) and employing a fully temperature dependent numerical solution scheme should improve results. Nonetheless, selection of a sufficient span of $D_c$ is still required and could prove challenging depending on the doping level and growth conditions. Indeed, as described above, for a doping level in the range of $10^{14}$–$10^{15}$ cm$^{-3}$, it was difficult to find NWs thick enough to yield nonzero dark current. On the other extreme, a $n$-type GaN NW doped at $n = 10^{18}$ cm$^{-3}$ with $\phi_m = 0.3$ V would be completely depleted for $D_m = 50$ nm, and the growth conditions may not yield a sufficient distribution of diameters in this range.

The simulations of photoconductive decay illustrate that relatively small uncertainties in $N_d$ (factors of 2) can result in much larger uncertainties in $\sigma_n$. Consequently, it is difficult to directly compare our estimated results for $\sigma_n$ with those of Ref. 37 even though the formal analysis is quite similar. Additionally, the uncertainty encountered in setting the normalization of the photocurrent decay compounds these problems, as illustrated in Figs. 12(a)–12(d). Therefore, the theoretically obtainable fits that should return unique values of $N_d$ and $\sigma_n$, as described in the Appendix, are not obtained in practice; however, one can use this analysis to place bounds on these quantities. In this manner we were able to estimate that $3 \times 10^{16}$ cm$^{-3} < N_d < 6 \times 10^{16}$ cm$^{-3}$ for batch B738 and then use the data of Fig. 9 to determine that $\mu$ should fall into the range of 500–700 cm$^2$/Vs as one might anticipate for low defect density MBE grown GaN.

We acknowledge the possibility that variations in carrier concentration between wires or within wires from a single growth run could certainly exist. However, the general trends illustrating the variation in conductivity with diameter (both herein and in Ref. 20) suggest that this is a secondary effect if it occurs.

The subgap PC was observed on samples before and after ALD coating with Al$_2$O$_3$. The intensity illuminating the samples at these wavelengths (380, 400, and 550 nm) was within a factor of 2–3 of that available at 360 nm. Several minutes were typically required for the photocurrent to reach equilibrium under constant illumination at these wave-lengths. By contrast, PC under 360 nm illumination would generally rise to a maximum level within a few seconds for uncoated NWs. Figures 13(a) and 13(b) illustrate that the decay time of the PPC was comparable for all excitation wavelengths prior to ALD coating. This suggests that the same decay process (e.g., photogenerated holes trapped on the surface recombining with conduction electrons thermionically emitted from the neutral region) is responsible in all cases. Armstrong et al. argued that subgap PC should be dominated by majority carrier photoemission from a deep level within the depletion region. Here, the photogenerated electron emitted into the conduction band would be pulled into the neutral region and the remaining positive charge would partially screen the depletion field since it is in the immediate vicinity of the surface.

If this mechanism were dominant we would not necessarily expect the same decay time as observed for 360 nm excitation nor would we expect to see an increase in decay time following ALD coating. However, uncoated NWs show roughly the same PPC decay times when excited above or below gap and PPC decay times always increase after ALD Al$_2$O$_3$ coating for all excitation wavelengths considered. These observations suggest that the surface plays the dominant role and that subgap excitation produces mobile holes via transitions to intermediate trap and/or defect levels. This process would first involve majority carrier photoemission of a deep level, as suggested in Ref. 18, followed by photoexcitation of an electron from the valence band to the same deep level, thus leaving a mobile hole available to be swept to the surface and participate in screening the depletion field.

While such defect/trap states plausibly explain the observed subgap PC within the context of our model, we saw no evidence of midgap “yellow band” PL from these NWs. PL was performed at 16 and 300 K on samples 2, 4, 6, and 8 (prior to Al$_2$O$_3$ ALD coating) and on various single NW samples from both growth runs before and after ALD alumina coating. In no cases did we observe below-gap PL emission. Finally, we also remark that we do not observe

![FIG. 17. 3D map of the least-squared solution of Eq. (4) using as input data the hypothetical case illustrated in Fig. 11(b) with $D_m=350$ nm, $N_d=5 \times 10^{16}$ cm$^{-3}$, and $\sigma_n=1 \times 10^{-21}$ cm$^2$. The map is scaled such that $N_d$ ranges from $4.5 \times 10^{16}$ to $5.5 \times 10^{16}$ cm$^{-3}$ and $\sigma_n$ ranges from $5 \times 10^{-21}$ to $1.48 \times 10^{-21}$ cm$^2$. The vertical axis is the negative logarithm of the least-squared deviation between the input and computed normalized photoconductive decay and is arbitrarily truncated at a value of 30. The pole conforms to a solution coincident with the values of $N_d$ and $\sigma_n$ used to generate the input data. The locus of minima appearing as a continuous “ridge” traversing diagonally across the map conforms to the solution of the limiting case where $\Phi(t) \rightarrow \phi_m$.](image)
sensitivity of the photocurrent to polarization of the excitation light, as has been reported in other GaN NW photoconduction studies. \footnote{Y. Huang, X. Duan, Y. Cui, and C. M. Lieber, \textit{Nano Lett.} \textbf{2}, 101 (2002).}

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**APPENDIX: DISCUSSION OF THE UNIQUENESS OF THE PHOTOCONDUCTIVE DECAY FITTING PROCEDURE**

We examine the problem of fitting photoconductive decay data as a method to recover unique values of \(N_d\) and \(\sigma_n\). This is motivated by the concern that as the decay approaches equilibrium and \(\Phi(t) \to \phi_m\), the process can be represented by a characteristic lifetime \(\tau_d\), where

\[
\tau_d = (N_d C_n)^{-1} \exp(\phi_m/kT) \tag{A1}
\]

and \(\phi_m\) is proportional to \(N_d\) via Eq. (1). In this limit an entire locus of \(N_d\) and \(C_n\) (and \(\sigma_n\)) exists as permissible solutions for a single measured value of \(\tau_d\). This suggests the need to fit all of the available decay data such that \(\Phi(t) < \phi_m\) subject to the constraint \([R_m - r_c(t_c)] \) is greater than roughly 4–5\(L\) in an effort to escape ambiguous solutions.

As an example, we use as input data the hypothetical case illustrated in Fig. 11(b) where \(N_d = 5 \times 10^{16} \text{ cm}^{-3}\) and \(\sigma_n = 1 \times 10^{-21} \text{ cm}^2\) were used to compute the decay of the normalized photocurrent. We then fit these data using a least-squares routine that searches for the minimum squared deviation between the data and the solution of Eq. (4) over a span of \(N_d\) and \(\sigma_n\). The result is illustrated in the respective three dimensional (3D) and shaded plan view relief maps of Figs. 17 and 18. The \(x\) and \(y\) axes are the respective scaled ranges of \(N_d\) and \(\sigma_n\) and the \(z\) axis is proportional to the logarithm of the sum-squared deviation. The topography of the map reveals that the expected solution \((N_d = 5 \times 10^{16} \text{ cm}^{-3} \text{ and } \sigma_n = 1 \times 10^{-21} \text{ cm}^2)\) appears as a pole, but that there is also a continuous remnant local minimum appearing as a locus satisfying Eq. (A1) for the special case under consideration (with \(\tau_d = 90.12 \text{ s}\) for this hypothetical example). The dashed curve appearing in Fig. 18 is a separate computed solution of Eq. (A1) superimposed on the relief map to illustrate that the remnant continuous minimum revealed from the least-squares fitting procedure indeed conforms to the limiting case represented by the solution of Eq. (A1). This result also demonstrates that the efficiency of the least-squares fitting procedure can be substantially improved by restricting the search grid of \(N_d\) and \(\sigma_n\) to only follow a band of these parameters in the vicinity of the remnant solution.
