Supporting Information : Non-contact measurement of charge carrier lifetime and mobility in GaN nanowires

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Bulk optical parameters for GaN

The terahertz frequency absorption and refractive index of reference semi-insulating c-plane GaN (purchased from *Kyma Technologies inc.*) is shown in Figure 1. It can be seen that our reference sample has little terahertz-frequency absorption and a frequency-independent refractive index of $3 \pm 1\%$.

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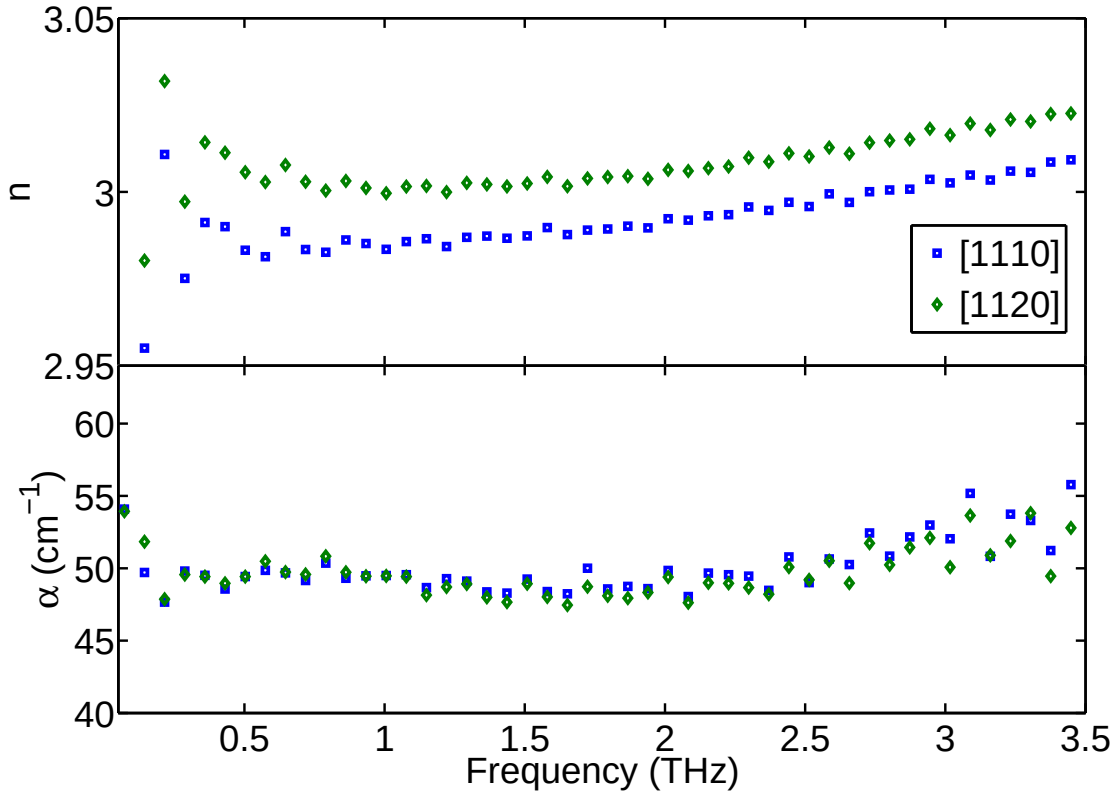

Figure 1: The equilibrium (non-photoexcited) refractive index n and absorption α of the bulk GaN sample for THz electric-field aligned along two crystal orientations, [1110] and [1120] represented as blue squares and green diamonds respectively.

Power dependent carrier lifetime in bulk GaN

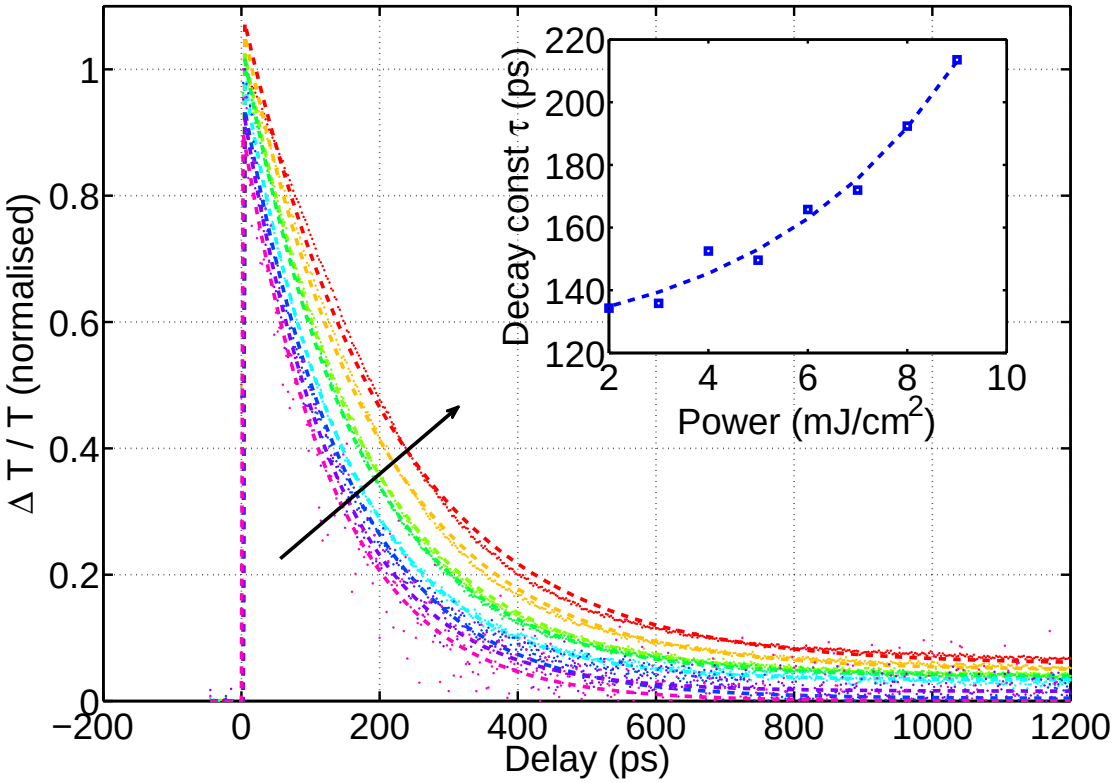

Figure 2: The normalised fluence-dependent carrier lifetime in bulk GaN (points). Lines are a monoexponential-fit to the data. The inset figure shows the variation in extracted carrier lifetime with incident laser power.

The power-dependent photoconductivity lifetime was measured for the bulk GaN sample for illumination of 2 mJ/cm^2 to 10 mJ/cm^2. Note the increasing lifetime with increasing fluence (directed along the arrow), which may arise due to trap saturation. The inset shows the monoexponential carrier lifetime extracted from an offset exponential fit to the data (dashed lines on main plot). The dashed line in the inset is a guide to the eye.

Extracting photoconductivity

This section outlines how photoconductivity, $\Delta\sigma$, is extracted from our measurement of $\frac{\Delta T}{T}$. We consider the nanowires to be confined within a layer of thickness, δ, occupying a fraction, f_{w}, of this layer, and surrounded by vacuum. Using SEM images of the measured sample, we determined δ and f_{w}. With these values we can convert the measured $\frac{\Delta T}{T}$ to $\Delta\sigma$ using

$$\Delta\sigma = \varepsilon_0 (A-1)\left[\frac{2c}{\delta} - i\omega(1+\varepsilon_{\mathrm{w}})\right], \tag{1}$$

and

$$A = \frac{1}{\frac{1}{f_{\mathrm{w}}}\frac{\Delta T}{T}+1}. \tag{2}$$

where ω is the frequency, c is the speed of light in vacuum, ε_0 is the permittivity of free space and ε_{w} is the static dielectric constant of GaN without photoexcitation.

Equations (1) and (2) were derived considering E_{on} and E_{off}, which are respectively the transmitted electric fields with and without the optical pump. These are defined as

$$E_{\mathrm{on}} = f_{\mathrm{w}}E_{\mathrm{w}^*} + (1-f_{\mathrm{w}})E_{\mathrm{v}} \tag{3}$$

$$E_{\mathrm{off}} = f_{\mathrm{w}}E_{\mathrm{w}} + (1-f_{\mathrm{w}})E_{\mathrm{v}}, \tag{4}$$

where E_{w} and E_{v} are the transmitted terahertz electric fields through the nanowires and the surrounding vacuum, respectively, and * indicates a photoexcited state. Combining Equations (3) and (4) gives

$$\frac{E_{\mathrm{w}^*}}{E_{\mathrm{w}}} = \frac{\Delta T}{T}\left[1+\left(\frac{1}{f_{\mathrm{w}}}-1\right)\frac{E_{\mathrm{v}}}{E_{\mathrm{w}}}\right]+1, \tag{5}$$

where $\Delta T = E_{\mathrm{on}} - E_{\mathrm{off}}$ and $T = E_{\mathrm{off}}$. The terahertz experiment directly measures $\frac{\Delta T}{T}$ where ΔT is the photoinduced change in terahertz probe transmission and T is the terahertz probe transmission in the absence of photoexcitation.

At terahertz frequencies the thin film limit is valid because $\frac{n\omega\delta}{c} \ll 1$. In the thin film limit we can make the approximation $\frac{E_\mathrm{v}}{E_\mathrm{w}} = 1$. Using this approximation and rearranging Equation (5), we define parameter A as

$$A = \frac{E_\mathrm{w}}{E_{\mathrm{w}^*}} = \frac{1}{\frac{1}{f_\mathrm{w}}\frac{\Delta T}{T} + 1}, \tag{6}$$

as in Equation (2).

The electric fields E_v, E_w and E_{w^*} may then be written as

$$E_\mathrm{v} = e^{in_\mathrm{v}\omega\delta/c}E_\mathrm{i} \tag{7}$$

$$E_\mathrm{w} = t_\mathrm{vw}t_\mathrm{wv}e^{in_\mathrm{w}\omega\delta/c}\mathrm{FP}_\mathrm{vwv}E_\mathrm{i} \tag{8}$$

$$E_{\mathrm{w}^*} = t_{\mathrm{vw}^*}t_{\mathrm{w}^*\mathrm{v}}e^{in_{\mathrm{w}^*}\omega\delta/c}\mathrm{FP}_{\mathrm{vw}^*\mathrm{v}}E_\mathrm{i}, \tag{9}$$

where FP_{ijk} are the Fabry-Pérot terms, t_{ij} are the Fresnel transmission coefficients, and n_{w^*} and n_w are the refractive indices of nanowires with and without photoexcitation, respectively. Substituting the appropriate forms of FP_{ijk} and t_{ij} into Equations (7) to (9) and applying the thin film limit $e^{in\omega\delta/c} = 1 + in\omega\delta/c$ gives

$$\frac{E_{\mathrm{w}^*}}{E_\mathrm{w}} = \frac{2 - \frac{i\omega\delta}{c}(1+n_\mathrm{w}^2)}{2 - \frac{i\omega\delta}{c}(1+n_{\mathrm{w}^*}^2)}. \tag{10}$$

Using the relation $\varepsilon = n^2$ in Equation (10), and rearranging, gives

$$\varepsilon_{\mathrm{w}^*} = \left[-\frac{E_\mathrm{w}}{E_{\mathrm{w}^*}}\left(2\frac{c}{i\omega\delta} - (1+\varepsilon_\mathrm{w})\right) + 2\frac{c}{i\omega\delta} - 1\right], \tag{11}$$

where $\varepsilon_{\mathrm{w}^*}$ and ε_w are the dielectric constants of the nanowires with and without photoexcitation, respectively. The photoinduced conductivity, $\Delta\sigma$, is given by

$$\varepsilon_{\mathrm{w}^*} = \varepsilon_\mathrm{w} + \frac{i\Delta\sigma}{\omega\varepsilon_0}. \tag{12}$$

Substituting Equation (11) into Equation (12) gives Equation (1) for $\Delta\sigma$ in terms of the measured signal $\frac{\Delta T}{T}$.

Modelling photoconductivity spectra

For an arbitrary mobility model, considering a single charge carrier species, the frequency-dependent change in free-carrier conductivity upon photoexcitation of a semiconductor may be represented as:

$$\Delta\sigma(\omega) = (N_{\mathrm{eq}} + \Delta N)e\mu\left(\omega, N_{\mathrm{eq}} + \Delta N\right) - N_{\mathrm{eq}}e\mu\left(\omega, N_{\mathrm{eq}}\right), \tag{13}$$

where ΔN and N_{eq} are the photogenerated charge density and equilibrium (background) charge density, respectively, and μ is the carrier mobility – a function of the frequency and instantaneous carrier density. For the case of the Drude model, the mobility is not a strong function of carrier density, with the exception of very-high-excitation density where scattering rates may be dominated by carrier-carrier scattering. However, when a plasma or plasmonic resonance is considered, the mobility has a peak (and zero-crossing in the imaginary component) at a non-zero frequency set by the carrier density, and hence a strong carrier-density dependence. In our model,[1,2] the photoinduced change in conductivity is attributed to a combination of surface plasmonic and free-carrier (Drude-like) components, with each component given by

$$\sigma_{\mathrm{Drude}}(\omega, N, \Gamma) = \frac{iNe^2\omega}{m^*\left(\omega^2 + i\omega\Gamma\right)} \tag{14}$$

$$\sigma_{\mathrm{Plasmon}}(\omega, N, \Gamma) = \frac{iNe^2\omega}{m^*\left(\omega^2 - \omega_{\mathrm{PL}}(N)^2 + i\omega\Gamma\right)}, \tag{15}$$

where m^* is the effective mass of the carriers (set to $0.23m_e$[3–5]). The plasmon frequency $\omega_{\mathrm{PL}}(N)$ is given by $\sqrt{fNe^2/m^*\varepsilon_r}$, with f being a geometrical factor equal to 1/2 for the case of a cylinder,[6] and where ε_r is the electric permittivity of the material (set to 9.4[7]).

It is important to note that owing to the small diameter of the nanowires ($\sim$0.3 μm) compared

with the wavelength of THz light ($\sim$300 μm), surface plasmons are excited in nanowires from THz photons propagating in free-space via subwavelength scattering.[8]

The data presented in Figure 3 of the main text may be fitted by combining Equations (13) to (15). The equilibrium carrier density is set at 1×10^{17} cm^{-3}, as determined by Raman measurements on a sample from the same growth run.[9] As the photogenerated carrier density is expected (and measured) to be lower than this, the introduction of extra carriers represents a small perturbation, and the carrier scattering rate Γ may be fixed for both equilibrium and photoinjected carriers. The equilibrium carrier density is divided between Drude-like and plasmon-like modes with a ratio ρ and $(1-\rho)$, respectively, while the photocarriers are divided with respective ratios ν and $(1-\nu)$. The measured conductivity may then be given as

$$\begin{aligned}\Delta\sigma(\omega) = &\left[\sigma_{\text{Drude}}\left(\omega, \rho N_{\text{eq}} + \nu\Delta N, \Gamma\right) + \sigma_{\text{Plasmon}}\left(\omega, (1-\rho)N_{\text{eq}} + (1-\nu)\Delta N, \Gamma\right)\right] - \\ &\left[\sigma_{\text{Drude}}\left(\omega, \rho N_{\text{eq}}, \Gamma\right) + \sigma_{\text{Plasmon}}\left(\omega, (1-\rho)N_{\text{eq}}, \Gamma\right)\right], \end{aligned} \tag{16}$$

By examining the equation for Drude conductivity given in Eqn. (2), it can be seen that it is possible to expand $\sigma(\omega, N_{\text{eq}} + \Delta N, \Gamma)$ into $\sigma(\omega, N_{\text{eq}}, \Gamma) + \sigma(\omega, \Delta N, \Gamma)$, and hence simplify Eqn. (4) to

$$\begin{aligned}\Delta\sigma(\omega) = &\left[\sigma_{\text{Drude}}\left(\omega, \nu\Delta N, \Gamma\right) + \sigma_{\text{Plasmon}}\left(\omega, (1-\rho)N_{\text{eq}} + (1-\nu)\Delta N, \Gamma\right)\right] - \\ &\sigma_{\text{Plasmon}}\left(\omega, (1-\rho)N_{\text{eq}}, \Gamma\right) \end{aligned} \tag{17}$$

with free parameters ΔN, ρ, ν, and Γ. This is the equation used to fit Figure 3 in the main text; best-fit parameters are given in Table 1. To convert from angular frequency, ω (in Equations (13) - (17)), to linear frequency, ν (in the figures and numerical results), use the relation $\nu(\text{Hz}) = \omega(\text{radian/s})/2\pi$.

Table 1: Best fit values for the model in Equation (17) to the experimental data

Parameter	**10ps Value**	**1000ps Value**
ΔN	$3.4 \times 10^{16}\text{cm}^{-3}$	$1.8 \times 10^{16}\text{cm}^{-3}$
ρ	56%	31%
ν	15%	15%
Γ	$9.3 \times 10^{12}\text{s}^{-1}$	$9.3 \times 10^{12}\text{s}^{-1}$

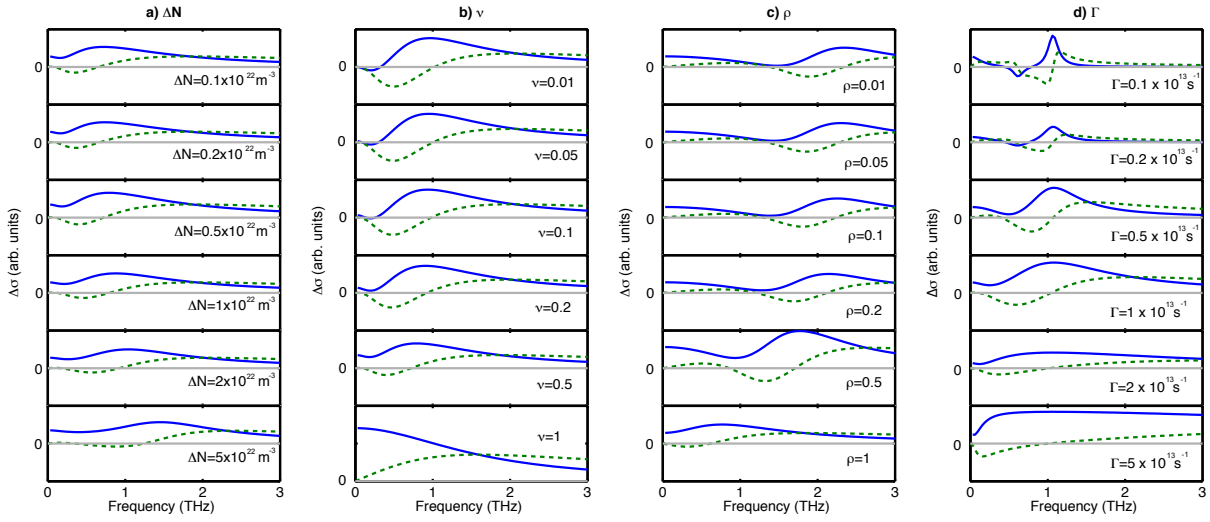

Figure 3: The effect of varying the (a) Total photoinjected carrier density, (b) Drude component of photoinjected carriers, (c) Drude component of background carriers and (d) scattering rate (Γ) within the model presented is shown. In each case the values of the parameters that are not being varied are those given in Table 1. The solid blue line (dashed green line) represents the real (imaginary) part of the photoconductivity, respectively.

Exploration of parameter space

Figure 3 explicitly shows the effect of varying each of the four parameters. Note that the absolute size of each spectrum shown varies; they are displayed on different scales for clarity. However, the true, unscaled value is used for fitting purposes. As can be seen in Fig. (Figure 3a), increasing the carrier density causes an expected shift in the resonance position to higher frequencies, with no appreciable change in shape at low frequencies. Varying the parameter ν (Figure 3b) causes a change in the low-frequency response, due to the increased free-carrier response at large values of ν; for $\nu = 1$, only a purely Drude-like response can be observed. The effect of varying ρ — the proportion of background carriers in a surface-plasmonic mode — is shown in Figure 3c. It can be seen that for low values (where the majority of background carriers are in a plasmonic mode), the resonance peak of the photoinjected carriers is shifted to higher frequency, without increasing the full-width-at-half-maximum, while at low values the 'traditional' Drude plus plasmonic response is evident. Finally, varying the scattering rate has the typical effect on plasmonic peak width. It can be seen that each of these parameters has a different set of effects upon the spectral conductivity, permitting relatively straightforward modelling.

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