Supporting Information

Experimental Details

GaAs nanowires were grown on z-cut quartz substrates using the vapour-liquid-solid mechanism and employing gold nanoparticles as a catalyst, following the technique outlined in Refs. 14 and 15 of the manuscript. The experimental arrangement is typical for THz-TDS; briefly, a 1mJ 40fs 800nm pulse from a 1kHz amplified Ti:Sapphire laser [Spectra-Physics *Spitfire Pro*] is split into three pathways. Approximately 250μJ of this is used as an optical pump to photoinject carriers, 2μJ is taken as a gate in the free space electro-optic detection and the remaining 700μJ is used to generate a single cycle of THz radiation using optical rectification in a 2mm thick ZnTe crystal. This pulse is utilized to probe the electronic properties of the sample, and is detected through free space electro-optic sampling at a second ZnTe crystal. By altering the delay between the optical pump, the terahertz probe, and the optical gate pulse, a 2-dimensional map can be created, providing the full time-resolved spectral response of the photoexcited material. Experiments were carried out at room temperature under vacuum ($< 10^{-3}$ mbar) in order to eliminate water vapour from the terahertz path and oxidisation of the sample. A dual lock-in amplifier method was employed to measure the small changes induced in the terahertz transmission.

Thin-film model

The photoinduced conductivity $\Delta\sigma(\omega)$ for a medium consisting of an area fraction f_s of nanowires (and

$$\Delta\sigma(\omega) = \frac{\omega\epsilon_0}{i}\left[\frac{c}{i\omega\delta}\left(2 - \frac{i\omega\delta}{c} - C\left(2 - \frac{i\omega\delta(1+\epsilon)}{c}\right)\right) - \epsilon\right]$$

1- f_s of vacuum) can be calculated via the following expression:
where

$$C = \frac{1}{\frac{1}{f_s}\frac{\Delta T}{T_{\mathrm{off}}}\left(f_s + \frac{T_r}{T_s}(1 - f_s)\right) + 1}$$

In these expressions, T_{on} and T_{off} are the measured terahertz electric field transmitted through the sample with and without the pump beam, and $\Delta T = T_{on} - T_{off}$. T_s is the terahertz electric field after transmission through a single non-photoexcited nanowire (of thickness δ and dielectric function ε), and T_r is the electric field after the same thickness of vacuum. For semi-insulating GaAs $T_s/T_r = 0.67$ over the frequency range 0-3THz, owing to the Fresnel transmission coefficients. The most critical parameter determining the electronic behaviour of the nanowires is the carrier density, which is defined by the optical pump fluence and the geometrical alignment of the nanowires. The nanowires posses a distribution of sizes and orientations – the angle between the nanowire and the plane of polarization of the terahertz probe determines whether the nanowire exhibits free-carrier-like or LSP-like behaviour (Inset to Figure 1, i) and ii)). Nanowires at a larger angle from the surface normal present a greater surface area to the terahertz probe beam, and therefore dominate the response of the sample. For this reason, an effective thin film thickness of δ = 50nm is used in the above calculation, reflecting the predominant top-width of the nanowires. While the diameter of the nanowires shows some variation (it increases towards the base) this effect is not as critical as the variation in carrier density due to the distribution of nanowire angles from the surface normal. Our analysis takes into account the distribution in carrier densities from the latter, which has the effect of slightly broadening the features in the frequency-dependent conductivity. The distribution of axial lengths has no impact upon the thin-film thickness or carrier density, and is therefore neglected in our analysis.