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# Ultralow Surface Recombination Velocity in InP Nanowires Probed by Terahertz Spectroscopy

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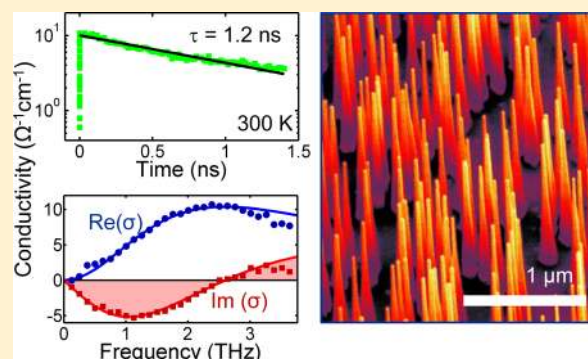
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## S Supporting Information

**ABSTRACT:** Using transient terahertz photoconductivity measurements, we have made noncontact, room temperature measurements of the ultrafast charge carrier dynamics in InP nanowires. InP nanowires exhibited a very long photoconductivity lifetime of over 1 ns, and carrier lifetimes were remarkably insensitive to surface states despite the large nanowire surface area-to-volume ratio. An exceptionally low surface recombination velocity (170 cm/s) was recorded at room temperature. These results suggest that InP nanowires are prime candidates for optoelectronic devices, particularly photovoltaic devices, without the need for surface passivation. We found that the carrier mobility is not limited by nanowire diameter but is strongly limited by the presence of planar crystallographic defects such as stacking faults in these predominantly wurtzite nanowires. These findings show the great potential of very narrow InP nanowires for electronic devices but indicate that improvements in the crystallographic uniformity of InP nanowires will be critical for future nanowire device engineering.

**KEYWORDS:** InP, nanowire, terahertz, photoconductivity, surface recombination velocity, mobility



Semiconductor nanowires are predicted to drive new generations of compact, ultrafast, and high efficiency electronic and optoelectronic devices. Among nanowire materials, InP is especially promising due to its direct band gap and high electron mobility. A multitude of prototype InP nanowire devices have been demonstrated including photo-detectors,<sup>1</sup> light-emitting diodes,<sup>2</sup> waveguides,<sup>3</sup> solar cells,<sup>4,5</sup> and field effect transistors.<sup>2,6</sup> Despite these early successes, there remain many fundamental unanswered questions concerning the dynamics of charge carriers in nanowires, and the effects of nanowire size, surfaces, and crystal structure on nanowire electronic properties. A greater understanding of these effects is essential for the future engineering of nanowire-based devices.

In this Letter, we examine the ultrafast carrier dynamics within InP nanowires and assess the effects of nanowire diameter, surfaces, and crystal structure. These investigations were performed using optical pump–terahertz probe (OPTP) spectroscopy, a technique which is ideally suited for nanowire studies because it is a noncontact ultrafast probe of room temperature photoconductivity with subpicosecond resolution.<sup>7</sup> The contact-free nature of this technique confers a significant

advantage over conventional electrical transport measurements, which are subject to artifacts associated with electrical contacts and the models used to extract data.<sup>8,9</sup> A further advantage is that the OPTP measurements are performed at room temperature, so its measurements of carrier mobility and lifetime are directly relevant to future InP nanowire-based devices which will be operated at room temperature.

From OPTP measurements on InP nanowires of different diameters, we determine that surface recombination is negligible in InP nanowires. This result is despite the large surface area-to-volume ratio intrinsic to the nanowires and contrasts strongly with studies of GaAs nanowires for which surface recombination severely limits the carrier lifetime.<sup>10</sup> For InP nanowires we measured a long photoconductivity lifetime of over 1 ns. The long carrier lifetime at room temperature and insensitivity to surface states suggests that InP nanowires are excellent candidates for optoelectronic devices, especially for photovoltaic devices. Time-resolved PL spectroscopy was

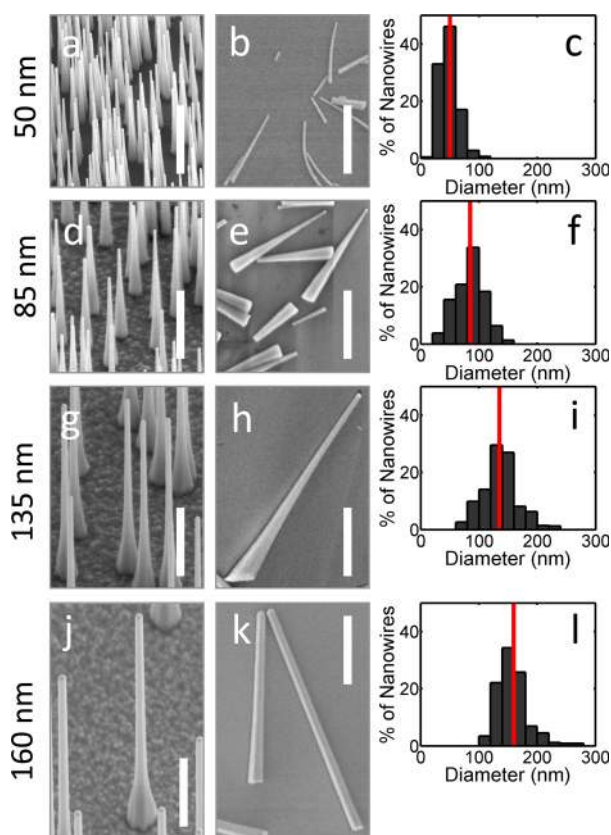
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performed in conjunction with OPTP measurements, and provided evidence that, after photoexcitation, electrons and holes are rapidly separated spatially into zinc-blende (ZB) and wurtzite (WZ) crystal sections, respectively, within the nanowires. This spatial separation of electrons and holes causes rapid PL quenching within 100 ps but allows a long carrier lifetime leading to long-lived photoconductivity. Additionally, we found that the carrier mobility does not show a simple systematic relationship with nanowire diameter. Instead, the carrier mobility is strongly influenced by the presence of planar crystallographic defects such as stacking faults, twins, and ZB–WZ polytypism in these predominantly WZ nanowires.

Nominally undoped InP nanowires were grown on InP (111)B substrates by metal–organic chemical vapor deposition (MOCVD) using Au nanoparticles to direct nanowire growth. Four samples were grown, each with Au nanoparticles of a particular nominal diameter (20, 30, 50, and 80 nm diameter). To eliminate the photoconductivity of the InP substrates, the nanowires were then transferred to z-cut quartz substrates by gently rubbing the two substrates together. Figure 1 illustrates scanning electron microscope (SEM) images of as-grown nanowires and nanowires on quartz. The nanowire diameters were measured from SEM images as described in the Supporting Information. The nanowire diameters depended on the diameter of the original Au nanoparticle plus a degree of tapering due to radial growth. Consequently each quartz

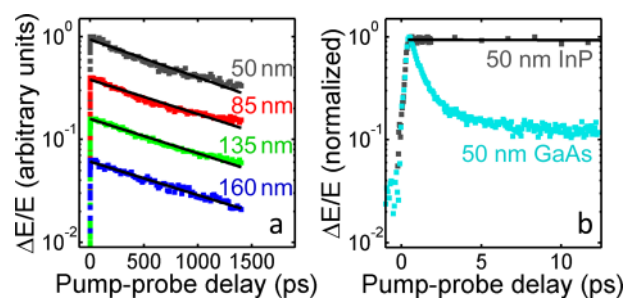


**Figure 1.** InP nanowires with average diameters of (a–c) 50 nm, (d–f) 85 nm, (g–i) 135 nm, and (j–l) 160 nm: a, d, g, and f are SEM images of InP nanowires as-grown on InP substrates at a tilt of 40°, b, e, h, and k are SEM images of InP nanowires transferred to quartz substrates, and c, f, i, and l are histograms of the diameters of nanowires on quartz. The average nanowire diameter for each sample is indicated in each histogram by the red line. SEM scale bars are 1  $\mu\text{m}$ .

substrate hosted a distribution of nanowire diameters as summarized in the histograms of Figure 1. We hereafter refer to the samples by their average nanowire diameter after transfer to quartz substrates: 50, 85, 135, and 160 nm which respectively grew from the 20, 30, 50, and 80 nm diameter Au nanoparticles. A comparison of these four samples allowed the effects of nanowire diameter and surface-to-volume ratio to be examined.

The dynamics of photoexcited carriers were measured using the optical pump–terahertz probe spectroscopy setup described in the Supporting Information. The nanowires on quartz substrates were photoexcited using a pump pulse centered at a wavelength of 800 nm with a duration of 35 fs and fluence between 1 and 160  $\mu\text{J}/\text{cm}^2$ . The photoexcitation induced a change  $\Delta E$  in the transmission of a weak terahertz probe pulse  $E$ ; this change in transmission is proportional to the photoinduced conductivity of the nanowires as discussed in the Supporting Information. Because the effective mass of holes in InP is significantly larger than that of electrons, we assume that the measured photoconductivity originated from photoexcited electrons only.

Nanowires have high surface area-to-volume ratios, and semiconductor surfaces tend to have high densities of dangling bonds which trap carriers and act as nonradiative recombination centers. Consequently, surface states are a major concern in nanowire engineering. Owing to the high aspect ratio of the nanowires, the sidefacets make the largest contribution to the surface area, whereas the top and bottom facets of the nanowires constitute only a minor portion of the nanowire surface (see Supporting Information). Nanowire diameter is the principal determinant of surface area-to-volume ratio. To assess the influence of surfaces on InP nanowires, we compare the photoconductivity lifetimes in each of the four samples of differing diameter, or equivalently, of differing surface-to-volume ratio. Figure 2a shows the decays of  $\Delta E/E$  with time



**Figure 2.** Pump-induced change in terahertz electric field ( $\Delta E/E$ ) at different pump–probe delays. (a)  $\Delta E/E$  decays for 50, 85, 135, and 160 nm diameter InP nanowires. These are scaled for clarity. (b)  $\Delta E/E$  decays for 50 nm diameter InP nanowires and 50 nm diameter GaAs nanowires. The photoexcitation pump fluence was 8  $\mu\text{J}/\text{cm}^2$ . Straight lines are monoexponential fits to the decays.

after photoexcitation for the four InP nanowire samples. The photoconductivity shows a rapid rise within 1 ps, followed by a slow decay. These data were fitted with an exponential function yielding time constants,  $\tau$ , of 1.18 ns, 1.27 ns, 1.30 ns, and 1.34 ns, respectively, for the 50, 85, 135, and 160 nm diameter nanowires. Even the lowest diameter nanowires with the highest surface-to-volume ratio show a long photoconductivity lifetime. The weak dependence of photoconductivity lifetime on nanowire surface-to-volume ratio indicates that the carrier lifetime in InP nanowires is relatively insensitive to surface

states. This is consistent with the low surface recombination velocity of the InP material system.<sup>11,12</sup> As derived previously<sup>13,14</sup> and described in the Supporting Information, the effective recombination time is closely approximated by the function:

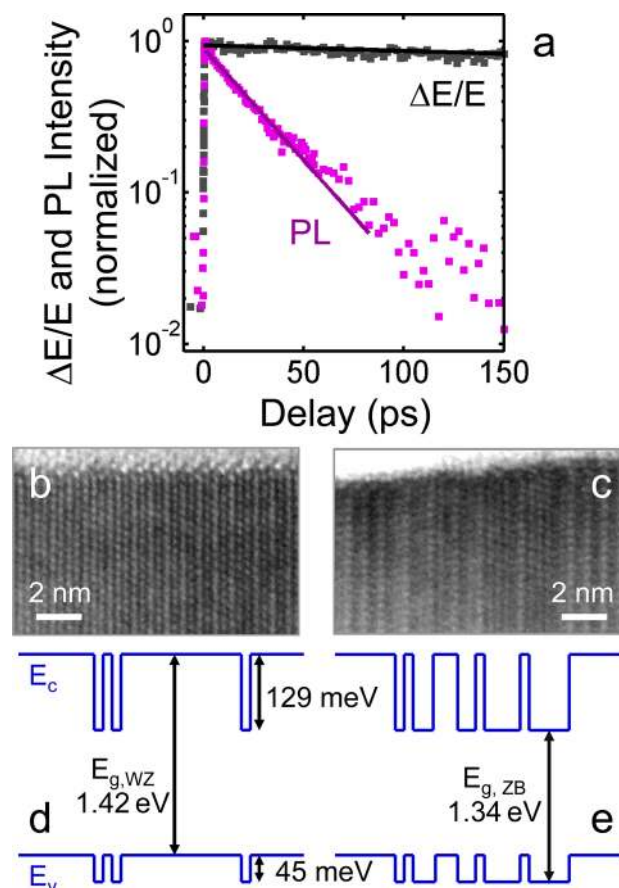
$$\frac{1}{\tau} = \frac{1}{\tau_{\text{volume}}} + \frac{4S}{d} \quad (1)$$

where  $d$  is the nanowire diameter,  $S$  is the surface recombination velocity, and  $\tau_{\text{volume}}$  is the time constant for recombination at volume defects. By fitting eq 1 to the experimental  $\tau$  values we extract a  $\tau_{\text{volume}}$  of 1.4 ns and a surface recombination velocity of only 170 cm/s. This surface recombination velocity is consistent with results obtained for bulk n-InP.<sup>11,15,16</sup>

This result contrasts markedly with GaAs nanowires, as demonstrated in Figure 2b. The GaAs nanowires studied were of similar diameter to the 50 nm diameter InP nanowires, but the GaAs nanowires exhibit an extremely rapid initial decay in photoconductivity due to carrier trapping at surface states.<sup>10</sup> This is consistent with the high surface recombination velocity of GaAs.<sup>12</sup> Generally, surface passivation is essential to improve carrier lifetimes in GaAs nanowires.<sup>17</sup> InP nanowires, on the other hand, exhibit prolonged photoconductivity and a remarkably low electron trapping rate at surfaces, even without surface passivation. These findings are significant for many electronic applications which require long carrier lifetimes. In photovoltaic devices, for example, the long carrier lifetime and low surface recombination velocity would minimize recombination losses, to maximize the collected current and maximize energy conversion efficiency. We note that surface passivation of InP nanowires may yet be advantageous for light emission applications and photodiode devices, as demonstrated in previous studies.<sup>5,18,19</sup>

To further examine the carrier lifetimes, we performed room temperature time-resolved PL measurements using a PL up-conversion setup described in the Supporting Information. The sample was excited at 736 nm with pulses of 100 fs duration. Emitted PL was detected at the peak of the PL spectrum, at 870 nm (1.43 eV). This corresponds approximately to the band gap of WZ InP at room temperature as measured experimentally.<sup>9,20,21</sup> Figure 3a plots both the decay of  $\Delta E/E$  and the decay of PL intensity for the same sample after photoexcitation with pulses of similar fluences. Interestingly, the PL decays rapidly with a decay time of only 30 ps, compared to the slow ( $>1$  ns) decay time of  $\Delta E/E$ .

This apparent discrepancy relates to the fundamental differences between OPTP and PL measurements. OPTP spectroscopy measures the nanowire conductivity, whereas in PL spectroscopy, the PL intensity is proportional to the product of the electron and hole density distributions. The long OPTP lifetime suggests that photoexcited conduction electrons are present beyond 1 ns. The rapid quenching of PL within 100 ps suggests that the photoexcited electrons and holes contributing to conduction are spatially separated on this time scale and thereafter experience only a low radiative recombination rate. One explanation for this spatial separation is band bending at nanowire surfaces (see Supporting Information), but this effect is negligible in intrinsic and n-doped InP nanowires,<sup>26</sup> consistent with the very low surface recombination velocity we measure. Therefore the most likely root of spatial separation is the WZ–ZB polytypism present in the nanowire. The high resolution TEM images of Figure 3b



**Figure 3.** (a) Comparison of  $\Delta E/E$  decay and time-resolved PL decay for 50 nm diameter InP nanowires. For all decays the photoexcitation pump fluence was approximately  $8 \mu\text{J}/\text{cm}^2$ . For PL measurements samples were photoexcited at 736 nm, and emitted PL was measured at 870 nm. For OPTP measurements samples were photoexcited at 800 nm. (b, c) HRTEM image of a typical InP nanowire (a) tip featuring predominantly WZ structure with stacking faults and (c) base with a higher density of stacking faults and thicker ZB segments. (d, e) Band diagrams at room temperature corresponding to nanowire (d) tip and (e) base. These band diagrams were constructed from published experimental and theoretical data for band gaps and band offsets.<sup>9,20–25</sup>

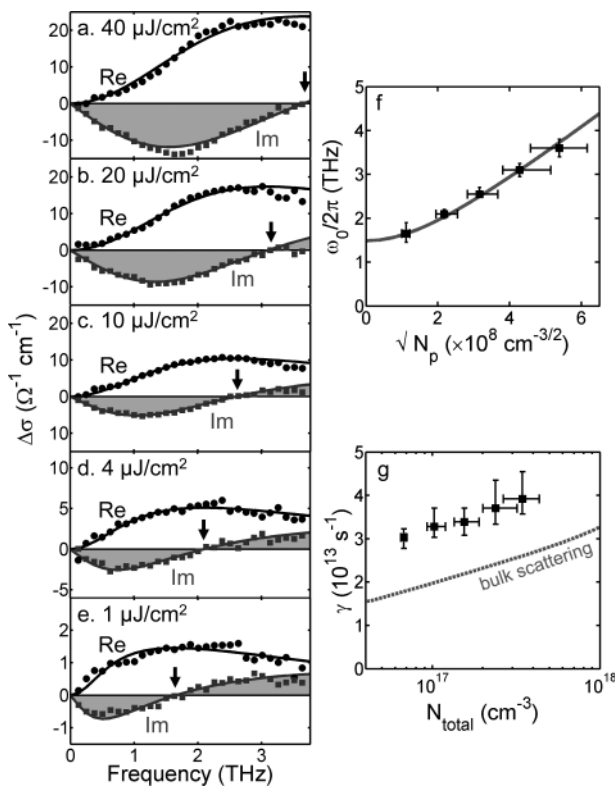
and c exemplify the crystal structure of these nanowires, which is predominantly WZ with thin ZB sections. These ZB sections vary in thickness between one bilayer (a single stacking fault) and up to eight bilayers. Nanowire tips exhibited lower densities of single stacking faults, whereas bases displayed a higher densities of stacking faults and thicker ZB sections. In WZ InP the conduction band is between 112 and 129 meV higher in energy, and the valence band is between 29 and 45 meV higher in energy than in ZB InP, as predicted theoretically<sup>23–25</sup> and observed experimentally.<sup>22</sup> This creates a type II junction between WZ and ZB sections of InP nanowires as illustrated in Figure 3d and e. After photoexcitation electrons and holes are rapidly separated into lower energy states in ZB and WZ sections, respectively. The spatial separation of electrons and holes causes a long carrier lifetime and low radiative recombination rate, consistent with our long OPTP lifetime and short PL lifetime. The short-lived PL we observe at 1.43 eV can be attributed to radiative recombination of electron–hole pairs residing in WZ sections of the nanowires, which is rapidly quenched due to localization of



electrons and holes into ZB and WZ sections, respectively. More long-lived red-shifted PL is expected from spatially separated electrons and holes, and this has been observed in low temperature PL measurements.<sup>27,28</sup>

Note that electrons and holes may still contribute to conduction despite their localization in ZB and WZ nanowire sections. In these predominantly WZ nanowires, the ZB segments are sufficiently thin, at less than 3 nm in thickness, that there is considerable leakage of the electron wave function into adjacent WZ segments.<sup>25</sup> The localization of electrons and holes could, however, result in increased scattering at boundaries between ZB and WZ segments and at stacking faults and consequently a reduced carrier mobility. To gain further insight into charge carrier scattering and mobility in these nanowires, we obtained photoconductivity spectra, as discussed in the following.

Figure 4 shows photoconductivity spectra collected for 50 nm InP nanowires. These were obtained at a delay of 20 ps after photoexcitation at various fluences. Spectra were also collected at various delays after photoexcitation, as presented in



**Figure 4.** Fluence dependence of terahertz conductivity of 50 nm InP nanowires at 20 ps after photoexcitation. (a–e) Photoinduced conductivity of with pump fluences of (a) 40, (b) 20, (c) 10, (d) 4, and (e) 1  $\mu\text{J}/\text{cm}^2$ . The symbols are the measured data, and the lines are the fitted plasmon responses. The real (circles and lines) and imaginary (squares and lines) components of the conductivity are plotted. The arrow indicates the resonant surface plasmon frequency  $\omega_0$ . (f) Surface plasmon frequencies  $\omega_0$  extracted from the fitted data (squares) and the fit (line) according to eq 3 with  $f = 0.5$  and background electron concentration  $N_d = 5.5 \times 10^{16} \text{ cm}^{-3}$ . (g) Carrier scattering rates  $\gamma$  extracted from the fitted nanowire data (squares) and theoretically predicted for bulk InP (dotted line). The error bars indicate the uncertainty in  $N_p$ ,  $N_{\text{total}}$ ,  $\omega_0$ , and  $\gamma$  resulting from uncertainty in the measured fill fraction and in the parameters giving the optimum fits.

the Supporting Information. The conductivity spectra feature a pronounced Lorentzian response. The resonance shifts to higher frequencies with increasing photoexcitation fluence, as indicated by the arrows in Figure 4a–e. This fluence dependence is typical of localized surface plasmon modes, for which the resonant frequency depends on carrier density and, therefore, fluence.<sup>29</sup> Other processes may also give Lorentzian responses, for example, excitonic transitions and quantum confined states; however these would not show resonance shifts with fluence. We therefore attribute the response to a surface plasmon mode. This is consistent with previous work on GaAs nanowires, which also exhibit surface plasmon modes in the terahertz range.<sup>10</sup> The conductivity spectra were accordingly fitted with the function

$$\sigma = \frac{iN_p e^2 \omega}{m_e^* (\omega^2 - \omega_0^2 + i\omega\gamma)} \quad (2)$$

where  $N_p$  is the photoexcited carrier density,  $e$  is the electronic charge,  $m_e^*$  is the electron effective mass,  $\omega_0$  is the surface plasmon resonance, and  $\gamma$  is the momentum scattering rate. For  $m_e^*$  we use the value for bulk ZB InP of  $0.08m_e$ . This assumption is reasonable because temperature-dependent PL studies suggest the electron and hole effective masses are similar in both ZB and WZ InP,<sup>21</sup> and theoretical studies predict similar effective masses for ZB and WZ.<sup>24,25,30</sup> Fitting eq 2 to the conductivity spectra allowed parameters  $N_p$ ,  $\omega_0$ , and  $\gamma$  to be extracted.

The extracted surface plasmon frequency,  $\omega_0$ , is plotted in Figure 4f, which clearly shows  $\omega_0$  shifts to higher frequencies with increasing carrier density. According to theory, the surface plasmon frequency is given by

$$\omega_0 = \sqrt{fN_{\text{total}}e^2/m_e^* \epsilon_r \epsilon_0} \quad (3)$$

where  $\epsilon_r$  is the dielectric constant of the InP nanowires at terahertz frequencies,  $\epsilon_0$  is the permittivity of free space, and  $f$  is a constant dependent on the nanowire geometry and the surrounding dielectric medium.<sup>31,32</sup> We choose  $m_e^*$  and  $\epsilon_r$  values for bulk ZB InP. Equation 3 closely fits the data using  $f = 0.5$  and assuming the total carrier density  $N_{\text{total}}$  is the sum of two components, the photoexcited carrier density  $N_p$  and a constant background carrier density  $N_d$  due to doping. The fit shown in Figure 4f yields a moderate doping density of  $N_d = 5.5 \times 10^{16} \text{ cm}^{-3}$ . Although these nanowires are nominally undoped, this doping level is reasonable because the surface states are donors,<sup>33</sup> which will contribute to the electron density in the nanowires, and because these nanowires were grown at a low temperature at which donors such as phosphorus antisite defects are easily incorporated.<sup>34</sup>

Figure 4g plots the extracted scattering rates,  $\gamma$ , which vary between  $3.0 \times 10^{13} \text{ s}^{-1}$  and  $3.8 \times 10^{13} \text{ s}^{-1}$ , with a higher frequency of scattering events at higher carrier densities. From the scattering times the carrier mobilities can be calculated via

$$\mu = \frac{e}{m_e^* \gamma} \quad (4)$$

The extracted  $\gamma$  correspond to mobilities between 570 and 730  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . These values are significantly lower than typical electron mobilities of 6000  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in high quality InP epilayers.<sup>35</sup> Our data therefore suggest that additional carrier scattering processes dominate the transport of electrons in nanowires compared to bulk.

In bulk InP at room temperature, the dominant scattering processes are carrier–phonon, carrier–carrier, carrier–plasmon, and carrier–impurity scattering. These mechanisms result in theoretical scattering rates shown in Figure 4g, which were calculated using models outlined in previous publications<sup>36,37</sup> and as described in the Supporting Information. Both the experimental  $\gamma$  for nanowires and the theoretical  $\gamma$  for bulk InP show a similar dependence on carrier density, primarily due to increased carrier–carrier scattering at higher carrier densities. The experimental  $\gamma$  are, however, higher by approximately  $1.3 \times 10^{13} \text{ s}^{-1}$ . This additional scattering component is constant, that is, not dependent on carrier density.

In nanowires, this additional scattering could arise from (i) roughness at nanowire surfaces and (ii) band offsets at planar crystallographic defects such as stacking faults, twins, and interfaces between ZB and WZ segments. To estimate the scattering contribution from (i), we refer to the model developed by Unuma et al. for quantum wells.<sup>38</sup> TEM images were analyzed from which we estimated the upper limit of the roughness height as 1 nm and estimated the lower limit of correlation length as 10 nm. This modeling revealed that surface roughness scattering is negligible for nanowire diameters larger than 20 nm, which is valid for all nanowire diameters studied here.

The modeling described above predicted that surface roughness scattering (i) has negligible influence on carrier mobility. This would imply that the nanowire surface area-to-volume ratio, and consequently diameter, should have a minimal effect on carrier mobility. To examine this prediction experimentally, we have measured photoconductivity spectra and extracted  $\gamma$  for the four samples of different diameters. The spectra are provided in the Supporting Information. For the 50, 85, 135, and 160 nm samples the scattering rates were approximately  $3.3 \times 10^{13} \text{ s}^{-1}$ ,  $18 \times 10^{13} \text{ s}^{-1}$ ,  $10 \times 10^{13} \text{ s}^{-1}$ , and  $4.5 \times 10^{13} \text{ s}^{-1}$ , respectively. These scattering rates correspond to mobilities of  $660 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $220 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $480 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively, for the 50, 85, 135, and 160 nm diameter samples. These mobilities show no systematic dependence on nanowire diameter: the 50 and 160 nm nanowires exhibit the highest mobilities, whereas the intermediate diameters exhibit the lowest mobilities. The nonsystematic variation in mobility suggests that other factors, for instance the density of stacking faults, plays a more dominant role in carrier dynamics than scattering at nanowire surfaces.

Assuming an electron thermal velocity of  $4.1 \times 10^7 \text{ cm/s}$ , the measured scattering rates correspond to average scattering lengths,  $\lambda$ , between 2.3 and 12 nm (see Supporting Information). These lengths are considerably lower than the nanowire diameters studied here, supporting our observation that scattering at nanowire surfaces is not the major mechanism limiting carrier mobility. These scattering lengths are, however, comparable to the distances between planar crystallographic defects, as seen in the TEM images of Figure 3.

The most likely explanation for the low mobility in these nanowires is, therefore, the high density of stacking faults (ii). Recent publications on transport measurements of InP nanowire field effect transistors have alternately proposed that mobility is significantly degraded by stacking faults<sup>8,39</sup> or by surface scattering.<sup>40</sup> These studies, however, did not compare nanowires of different diameters. Our diameter-dependent measurements and theoretical calculations exclude the

possibility of significant surface scattering, providing strong evidence that stacking faults limit nanowire conductivity.

The nonsystematic variation in mobility with nanowire diameter may be ascribed to differences in the density, distribution, and thickness of ZB segments from sample to sample. Such sample-to-sample variations in crystal structure are expected because the nanowire crystal structure is influenced by the nanowire diameter, and by a number of related parameters, such as nanowire growth rate and the density of Au nanoparticles on the substrate.<sup>41,42</sup> During nanowire growth these parameters act in conflicting ways to stabilize either ZB or WZ layers, so that the stacking fault density shows a complex dependency on nanowire diameter. TEM examination of the nanowire samples revealed that the density of stacking faults and thickness of ZB sections indeed varies between nanowires of different diameters but also varies substantially within individual nanowires. Nanowire bases exhibited higher densities of stacking faults and thicker ZB sections than nanowire tips. This large variability within individual nanowires precluded a complete quantitative analysis of how stacking fault density and ZB section thickness vary with nanowire diameter. Future contact-free measurements on InP nanowire samples (i) without planar crystallographic defects and (ii) with more well-defined defect densities should elucidate the dependence of mobility on stacking fault density and the thickness of ZB segments.

In this study, OPTP spectroscopy has revealed the effects of nanowire diameter, surfaces, and crystal structure on carrier dynamics in InP nanowires. Our measurements indicate that InP nanowire surfaces have only a weak influence on carrier lifetime, in marked contrast to GaAs nanowires. For InP nanowires the low surface recombination rate results in a long photoconductivity lifetime of over 1 ns, even without surface passivation. This long photoconductivity lifetime points to the immense technological potential of InP nanowires for future optoelectronic and photovoltaic devices. Furthermore, theoretical calculations and OPTP measurements demonstrated that InP nanowire surface roughness has a negligible effect on carrier mobility. The mobility is, however, significantly degraded by the presence of planar crystallographic defects. These defects are also responsible for the spatial separation of electrons and holes, which rapidly quenches nanowire PL. Future nanowire-based devices will therefore require very high crystal quality of constituent InP nanowires. This study shows the promise of even very narrow InP nanowires but emphasizes the importance of developing growth techniques to control InP nanowire crystal structure tightly and reproducibly.

## ■ ASSOCIATED CONTENT

### Supporting Information

Description of experiments (nanowire growth, electron microscopy, terahertz time-domain spectroscopy, photoluminescence up-conversion spectroscopy), calculations for determining average nanowire diameter, calculations of nanowire surface area, calculations for determining surface recombination velocity, calculations for converting terahertz transmission data to photoconductivity, discussion of band bending at nanowire surfaces, discussion of ZB/WZ band offsets and thermal excitation, discussion of the fluence dependence of photoconductivity decay rates, calculation of theoretical carrier scattering rates, photoconductivity spectra at various times after photoexcitation, photoconductivity spectra for different nanowire diameters, and a summary of nanowire transport

parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Wang, J. F.; Gudixsen, M. S.; Duan, X. F.; Cui, Y.; Lieber, C. M. *Science* **2001**, *293*, 1455–1457.
- (2) Duan, X. F.; Huang, Y.; Cui, Y.; Wang, J. F.; Lieber, C. M. *Nature* **2001**, *409*, 66–69.
- (3) Ding, Y.; Motohisa, J.; Hua, B.; Hara, S.; Fukui, T. *Nano Lett.* **2007**, *7*, 3598–3602.
- (4) Goto, H.; Nosaki, K.; Tomioka, K.; Hara, S.; Hiruma, K.; Motohisa, J.; Fukui, T. *Appl. Phys. Express* **2009**, *2*, 035004.
- (5) Novotny, C. J.; Yu, E. T.; Yu, P. K. L. *Nano Lett.* **2008**, *8*, 775–779.
- (6) Franceschi, S. D.; van Dam, J. A.; Bakkers, E. P. A. M.; Feiner, L. F.; Gurevich, L.; Kouwenhoven, L. P. *Appl. Phys. Lett.* **2003**, *83*, 344–346.
- (7) Joyce, H. J.; Gao, Q.; Tan, H. H.; Jagadish, C.; Kim, Y.; Zou, J.; Smith, L. M.; Jackson, H. E.; Yarrison-Rice, J. M.; Parkinson, P.; Johnston, M. B. *Prog. Quantum Electron.* **2011**, *35*, 23–75.
- (8) Wallentin, J.; Ek, M.; Wallenberg, L. R.; Samuelson, L.; Borgström, M. T. *Nano Lett.* **2012**, *12*, 151–155.
- (9) Maharjan, A.; Pemasiri, K.; Kumar, P.; Wade, A.; Smith, L. M.; Jackson, H. E.; Yarrison-Rice, J. M.; Kogan, A.; Paiman, S.; Gao, Q.; Tan, H. H.; Jagadish, C. *Appl. Phys. Lett.* **2009**, *94*, 193115.
- (10) Parkinson, P.; Lloyd-Hughes, J.; Gao, Q.; Tan, H. H.; Jagadish, C.; Johnston, M. B.; Herz, L. M. *Nano Lett.* **2007**, *7*, 2162–2165.
- (11) Casey, H. C.; Buehler, E. *Appl. Phys. Lett.* **1977**, *30*, 247–249.
- (12) Nolte, D. D. *Solid-State Electron.* **1990**, *33*, 295–298.
- (13) Léonard, F.; Talin, A. A.; Swartzentruber, B. S.; Picraux, S. T. *Phys. Rev. Lett.* **2009**, *102*, 106805.
- (14) Dan, Y.; Seo, K.; Takei, K.; Meza, J. H.; Javey, A.; Crozier, K. B. *Nano Lett.* **2011**, *11*, 2527–2532.
- (15) Diadiuk, V.; Groves, S. H.; Armiento, C. A.; Hurwitz, C. E. *Appl. Phys. Lett.* **1983**, *42*, 892–894.
- (16) Rosenwaks, Y.; Shapira, Y.; Huppert, D. *Appl. Phys. Lett.* **1990**, *57*, 2552–2554.
- (17) Parkinson, P.; Joyce, H. J.; Gao, Q.; Tan, H. H.; Zhang, X.; Zou, J.; Jagadish, C.; Herz, L. M.; Johnston, M. B. *Nano Lett.* **2009**, *9*, 3349–3353.
- (18) Mattila, M.; Hakkarainen, T.; Lipsanen, H.; Jiang, H.; Kauppinen, E. I. *Appl. Phys. Lett.* **2007**, *90*, 033101.
- (19) van Vugt; Veen, S. J.; Bakkers, E. P. A. M.; Roest, A. L.; Vanmaekelbergh, D. J. *Am. Chem. Soc.* **2005**, *127*, 12357–12362.
- (20) Mattila, M.; Hakkarainen, T.; Mulot, M.; Lipsanen, H. *Nanotechnology* **2006**, *17*, 1580–1583.
- (21) Mishra, A.; Titova, L. V.; Hoang, T. B.; Jackson, H. E.; Smith, L. M.; Yarrison-Rice, J. M.; Kim, Y.; Joyce, H. J.; Gao, Q.; Tan, H. H.; Jagadish, C. *Appl. Phys. Lett.* **2007**, *91*, 263104.
- (22) Bao, J.; Bell, D. C.; Capasso, F.; Wagner, J. B.; Mårtensson, T.; Trägårdh, J.; Samuelson, L. *Nano Lett.* **2008**, *8*, 836–841.
- (23) Murayama, M.; Nakayama, T. *Phys. Rev. B* **1994**, *49*, 4710–4724.
- (24) De, S.; Coleman, J. N. *ACS Nano* **2010**, *4*, 2713–2720.
- (25) Zhang, L.; Luo, J.; Zunger, A.; Akopian, N.; Zwiller, V.; Harmand, J. *Nano Lett.* **2010**, *10*, 4055–4060.
- (26) van Weert, M. H. M.; Wunnicke, O.; Roest, A. L.; Eijkemans, T. J.; Silov, A. Y.; Haverkort, J. E. M.; 't Hooft, G. W.; Bakkers, E. P. A. M. *Appl. Phys. Lett.* **2006**, *88*, 043109.
- (27) Pemasiri, K.; Montazeri, M.; Gass, R.; Smith, L. M.; Jackson, H. E.; Yarrison-Rice, J.; Paiman, S.; Gao, Q.; Tan, H. H.; Jagadish, C.; Zhang, X.; Zou, J. *Nano Lett.* **2009**, *9*, 648–654.
- (28) Akopian, N.; Patriarche, G.; Liu, L.; Harmand, J. C.; Zwiller, V. *Nano Lett.* **2010**, *10*, 1198–1201.
- (29) Nienhuys, H.-K.; Sundström, V. *Appl. Phys. Lett.* **2005**, *87*, 012101.
- (30) Jancu, J. M.; Gauthron, K.; Largeau, L.; Patriarche, G.; Harmand, J. C.; Voisin, P. *Appl. Phys. Lett.* **2010**, *97*, 041910.
- (31) Pitarke, J. M.; Silkin, V. M.; Chulkov, E. V.; Echenique, P. M. *Rep. Prog. Phys.* **2007**, *70*, 1–87.
- (32) Seletskiy, D. V.; Hasselbeck, M. P.; Cederberg, J. G.; Katzenmeyer, A.; Toimil-Molares, M. E.; Léonard, F.; Talin, A. A.; Sheik-Bahae, M. *Phys. Rev. B* **2011**, *84*, 115421.
- (33) Newman, N.; Spicer, W. E.; Kendelewicz, T.; Lindau, I. *J. Vac. Sci. Technol., B* **1986**, *4*, 931–938.
- (34) Dreszer, P.; Chen, W. M.; Seendripu, K.; Wolk, J. A.; Walukiewicz, W.; Liang, B. W.; Tu, C. W.; Weber, E. R. *Phys. Rev. B* **1993**, *47*, 4111–4114.
- (35) Razeghi, M.; Maurel, P.; Defour, M.; Omnes, F.; Neu, G.; Kozacki, A. *Appl. Phys. Lett.* **1988**, *52*, 117–119.
- (36) Yu, P. Y.; Cardona, M. *Fundamentals of Semiconductors*, 3rd ed.; Springer: Berlin, 2005.
- (37) Lloyd-Hughes, J. *Appl. Phys. Lett.* **2012**, *100*, 122103.
- (38) Unuma, T.; Yoshita, M.; Noda, T.; Sakaki, H.; Akiyama, H. *J. Appl. Phys.* **2003**, *93*, 1586–1597.
- (39) Storm, K.; Nylund, G.; Borgström, M.; Wallentin, J.; Fasth, C.; Thelander, C.; Samuelson, L. *Nano Lett.* **2011**, *11*, 1127–1130.
- (40) Borgström, M. T.; Norberg, E.; Wickert, P.; Nilsson, H. A.; Trägårdh, J.; Dick, K. A.; Statkute, G.; Ramvall, P.; Deppert, K.; Samuelson, L. *Nanotechnology* **2008**, *19*, 445602.
- (41) Paiman, S.; Gao, Q.; Tan, H. H.; Jagadish, C.; Pemasiri, K.; Montazeri, M.; Jackson, H. E.; Smith, L. M.; Yarrison-Rice, J. M.; Zhang, X.; Zou, J. *Nanotechnology* **2009**, *20*, 225606.
- (42) Paiman, S.; Gao, Q.; Joyce, H. J.; Kim, Y.; Tan, H. H.; Jagadish, C.; Zhang, X.; Guo, Y.; Zou, J. *J. Phys. D: Appl. Phys.* **2010**, *43*, 445402.