Supporting Information for:

Hot Electron Dynamics in InAs-AlAsSb Core-Shell Nanowires

Daniel Sandner\textsuperscript{1}, Hamidreza Esmaielpour\textsuperscript{2}, Fabio del Giudice\textsuperscript{2}, Steffen Meder\textsuperscript{2}, Matthias Nuber\textsuperscript{1}, Reinhard Kienberger\textsuperscript{1}, Gregor Koblmüller\textsuperscript{2} and Hristo Iglev\textsuperscript{1,*}

\textsuperscript{1} Chair for Laser and X-ray Physics, Physics Department, TUM School of Natural Sciences, Technical University of Munich, James-Franck-Str. 1, 85748 Garching, Germany

\textsuperscript{2} Walter Schottky Institute and Physics Department, TUM School of Natural Sciences, Technical University of Munich, Am Coulombwall 4, 85748 Garching, Germany

- Corresponding authors: E-Mail: hristo.iglev@tum.de; gregor.koblmueller@wsi.tum.de
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Section 1: Microscopic characterization of as-grown NWs

![Figure S1: SEM images of as-grown NW arrays on silicon. (a) shows bare, unpassivated InAs NWs with average diameters of ~120 nm (left) and ~70 nm (right), respectively, while (b) illustrates InAs-AlAsSb core-shell NWs containing NW cores with diameters of ~140 nm (left) and ~40 nm (right). The latter are overall shorter due to the reduced growth time necessary to realize very thin cores.](image)

All NWs were grown as periodic arrays on Si (111) substrate using selective-area molecular beam epitaxy (SA-MBE). To realize site-selective growth, the Si (111) substrates were prepatterned by nanoimprint lithography (NIL) or electron beam lithography (EBL) to create mask patterns with different pitches. Growth of the InAs NWs was then performed at a temperature of 520°C, In flux of 0.6 A/s, and As$_4$-BEP (beam equivalent pressure) of 4.5e-5 mbar. Scanning electron microscopy
(SEM) images of two bare (core-only) InAs NWs are shown in Fig. S1(a) after a growth duration of 60 min. Average NW diameters and lengths for the two respective samples are ~120-nm and ~4-5 µm (left), and ~70 nm and ~3-4 µm (right), respectively.

Regarding InAs-AlAsSb core-shell NWs, the NW cores are grown under the same conditions. One sample had identical core growth time of 60 min, resulting in ~140-nm thick and ~7-8 µm long InAs NW cores (Fig.S1(b), left), while for another sample the growth time was only 7.5 min to achieve very thin NW cores of ~40-nm diameter (Fig.S1(b), right). Due to the reduced growth time, the NWs are overall much shorter (<1 µm). The cores in both samples were overgrown for 30 min with an AlAsSb shell at growth temperature of 425 °C and for another 10 min with a GaSb cap layer to prevent oxidation of the AlAsSb. The Al and Ga fluxes were set at 0.5 A/s, and the Sb2-BEP was 1.2e-6 mbar. The As cell was set to conditions that yield an incorporated As-molar fraction of ~18% in the AlAsSb shell, which represents close lattice matching conditions with the InAs core. Under these growth conditions, the thicknesses of the AlAsSb (GaSb) shell (cap) layers grown in the radial direction are on the order of ~20-25 nm (~5-nm). Hence, the overall diameters of these core-shell NW samples appear by about ~50-60 nm thicker than their respective NW cores.

Section 2: Visible optical absorption

![Figure S2: UV-Vis absorbance spectra of NWs of several size after transfer to transparent Barium fluoride (BaF₂) windows.](image)
Figure S2 shows normalized absorbance spectra of NWs transferred to BaF$_2$ windows as measured by UV-Vis extinction spectroscopy. One observes a major peak for each sample. The spectral position of the resonance depends on the thickness, surface passivation, and does not coincide with an inter-band transition (~0.4 eV for InAs). Two trends are visible: first, thin NWs show a blue-shifted resonance compared to thick ones, under the same set of surface conditions. Secondly, in the presence of a shell, the resonance is redshifted. This could be a result of the altered refractive index induced by surface passivation$^3$. Similar absorption peaks have been observed in periodic NW arrays, but not in almost randomly dispersed NWs. Both observations could stem from surface plasmon resonances (SPR). In addition, we observe that passivation narrows the spectral width of the observed peaks as the defect density at the surface is reduced and plasmons are less damped.

Optical microscopy, presented in Figure S3a, shows that following mechanical transfer of NWs, most of the 140 nm-thick NWs with a shell kept a certain orientation. This is also reflected in UV-Vis and FTIR spectroscopy performed with linear polarized light, seen in Fig. S3b. One can see that certain absorption features are independent of the NW orientation (e.g. at 1.7 eV), while others (0.6 eV, 1.2 eV, 2.5 eV) depend clearly on the polarization of light relative to the NW axis.

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**Figure S3 a; Optical microscopy of 140 nm-thick NWs with shell after transfer to a barium fluoride substrate. Most NWs are orientated in the same direction. b; UV-Vis extinction measured with linear polarized light parallel and perpendicular to the majority NW axis**
Section 3: Analysis of mIR PL
Photoluminescence was acquired using a home-built setup. The laser source used for excitation is focused on the sample with an all reflective Cassegrain objective. The spotsize on the sample was 8-10 µm and illuminated 4-8 NWs. All graphs showing the influence of a parameter such as the excitation energy or intensity were measured at the same spot.

Figure S4: Luminescence of bulk InAs recorded at room temperature with the same fit applied as in the main text yielding a temperature of 315 ± 10 K.

Figure S4 shows luminescence of bulk InAs at room temperature. By applying the same fit to the high energy tail as in Figure 1a, we extract a carrier temperature of 315 ± 10 K. This indicates that InAs shows only small variations in α(E) and absolute carrier temperatures can be extracted with the simple equation: $I_{PL}(\hbar\omega) = A \exp(-\hbar\omega/k_B T_C)$. This does not necessarily hold true for InAs NWs by their wurtzite structure, however in the main text we compare carrier temperatures of a single material for excitation with two different energies. Therefore, a modulation of α(E) would alter the extracted temperature but cannot explain the difference in temperature observed for optical excitation with photons of 1.27 eV and 1.97 eV.
Figure S5: Power dependent luminescence spectra of 140 nm-thick InAs-AlAsSb NWs at 10 K.

Figure S5 shows luminescence spectra of passivated InAs NWs for several excitation intensities. One observes a clear blueshift of the peak position at increasing excitation power densities. This may be explained by a pile-up of electrons in the conduction band.

Figure S6: Power dependent luminescence spectra of 40 nm-thick InAs-AlAsSb NWs at 10 K.

Figure S6 shows luminescence spectra of passivated InAs NWs for a core diameter of 40 nm. Compared to 140 nm-thick NWs presented in Figure S5, only a small blueshift on the order of 40 meV is observed.
Section 4: Normalized TA spectra at various delays

Figure S7: Normalized nIR TA spectra of 120 nm thick InAs NWs (left) and 140 nm thick InAs-AlAsSb NWs (right) measured after excitation at 800 nm for several probe wavelengths. Data for core-shell NWs also shown in Figure 1b.

To demonstrate that the high energy tail of the photoinduced nIR bleaching does decay faster than bleaching at energies close to the bandgap, we show the TA spectra of pure and passivated InAs NWs in Figure S7 normalized at the smallest energy, where we observed the strongest bleaching for most curves.

Section 5: Estimation of photoexcited charge carrier intensity

To calculate the photoexcited carrier density we use the dielectric function of InAs reported in the literature. Optical microscopy shows that NWs lie flat on the substrate after transfer. Vertical stacking of multiple wires on top of each other is not observed. Using Beer-Lamberts Law, we obtain a photoexcited carrier density of $2 \cdot 10^{17}$ cm$^{-3}$ for a pump fluence of 1 $\mu$J/cm$^2$ (at a photon energy of 1.55 eV).

In a previous study, a classical electrodynamics simulations based on the finite difference time domain (FDTD) method was used. For a photon energy of 2.27 eV and a pump fluence of 5 $\mu$J/cm$^2$, carrier densities of $1.2 \cdot 10^{18}$ cm$^{-3}$ and $1.9 \cdot 10^{18}$ cm$^{-3}$ were calculated for light polarized perpendicular and parallel to the NW axis, respectively. Our method yields a comparable carrier density of $1.2 \cdot 10^{18}$ cm$^{-3}$ for the same excitation parameters. By the random orientation of the NWs in our experiment, we don’t observe an effect of the pump polarization.
Figure S8: nIR TA dynamics of 120 nm thick InAs NWs measured after excitation at 800 nm for several probe wavelengths. Data also shown in Figure 1b.

Figure S8 shows transient absorption measured for probe wavelengths above the bandgap. Excitation at 1.55 eV generates hot electrons which populate the conduction band. This reduces the difference in population between VB and CB compared to a sample which has not been excited. In consequence, the band absorption measured by the probe beam, is weakened (bleached) for the excited sample and we observe increased transmission. States high above CBM are only occupied for a short period of time and, as electron cool, transient absorption measured for large probe energies (short wavelengths) declines fast towards zero. Further, states probed at a large probe energy have only a small probability for occupation which creates smaller absolute TA signals compared to probe energies close to CBM.
Figure S9a: Simulated band absorption bleaching curves (as observed with the nIR probe) for several probe energies. Dashed lines are mono-exponential fits. b: Occupation probability of states depending on their energy, measured regarding the valence band maximum, for certain delays. The same function (exponential decay) for the electron temperature was used as in S6a.

Since decay times observed in transient near-infrared absorption strongly depend on the probe wavelength, we used Fermi-Dirac statistics to find the relation between probe energy and observed decay constants. For this simple model, we assume that the electron temperature is raised by a gaussian pulse to $T = 2500$ K at $t = 0$ and decays with a single exponential function of 10 ps lifetime to 300 K. We then calculate the occupation probability according to Fermi-Dirac statistics for consecutive time steps and transient absorption for several probe energies based on the diminished difference in population between CB and VB. Bandgap renormalization effects are not included.

Compared to our experiments, simulated transient absorption displayed in Fig S9a follows the same trends, namely lifetimes and amplitudes increase for smaller probe energies (larger probe wavelengths) (see Figure S8). Calculated transient absorption curves were fitted with single exponentials, this reveals that transient absorption measured at a probe energy of 0.7 eV underestimates the lifetime of hot electrons (6.2 ps decay time of TA compared to 10 ps for electron temperature). Fig S6b shows occupation probabilities for several delays depending on the energy of the state, measured relative to the VBM. Thermalization (meaning evolution from the excited non-thermal distribution into an ensemble that can be characterized by a temperature) is not shown as it requires a much more advanced model but is expected to be finished well within 100 fs. One can see that the electron distribution is increasingly narrowed to the CBM due to cooling. Excitation at 1.55 eV (yielding the initial temperature of 2500 K in our experiments) and the lowest lying state of the CB (below the bandgap due to surface band bending) are marked. Quantitative values for the down bending were extracted from Speckbacher et al.6.
Section 7: Inversion analysis of TA dynamics at 0.7 eV

To get more insight into the decay mechanisms of the transient bleaching observed at a probe energy of 0.7 eV, we performed an inversion analysis\(^7\). The transient signal is differentiated to access the decay rate. The decay rate is plotted in a log-log plot (see Figure S10) versus the transient signal which serves as a proxy for the carrier density. Smoothing with a Fourier filter was necessary prior to the differentiation to avoid sign flips by noise. Oscillations in the decay rate are the result of residual noise. A single linear fit was applied to each curve as the slope does not change significantly. Gradients of 1.35±0.03 and 1.15 ± 0.05 are extracted for core-shell NWs with diameters 140 nm and 40 nm, respectively. By the absence of a clear kink in the curves, it is likely that a single decay mechanism is relevant in the observed range and mono-exponential fits can be reasonably applied.

Figure S10: Decay rate of TA dynamics at 0.7 eV (c.f. Fig. 3a) for passivated NWs of various size plotted versus the transient signal. The excitation energy and fluence was 1.55 eV and 300 µJ/cm\(^2\), respectively.
Figure S11: Transient absorption of pure InAs NWs for a probe energy of 0.62 eV for different excitation energies and intensities. Dots represent raw data; solid lines show exponential fits.

Figure S11 shows transient absorption of pure InAs NWs at 1.55 and 3.1 eV (c.f. Fig 4a in the main text). One observes strong ground state bleaching by the photoexcited carriers because the probe energy is above the bandgap. Opposite to the passivated NWs shown in Fig 4a of the main text, we don’t observe a strong positive TA signal. The bleaching decays as carriers cool down to the conduction band minimum. A comparison between excitation at 1.55 eV and 3.1 eV shows that the minimum (strongest bleaching) is slightly delayed at around 3 ps. One explanation is that excitation at 3.1 eV creates significant side-valley populations. Previous studies reported carriers returning from the L- and X-valley to the Γ-valley on the few ps timescale. Overall, we observe slower cooling for excitation at excitation at 3.1 eV compared to 1.55 eV which can be explained by the larger excess energy that must be transferred to other carriers and the lattice. Mono-exponential fits were used to quantify the decay. A lifetime of 12.9 ± 0.3 ps is found for excitation at 1.55 eV. For an excitation energy of 3.1 eV, we find lifetimes of 20.8 ± 0.3 ps and 24.3 ± 0.5 ps for pump fluences of 140 µJ/cm² and 35 µJ/cm², respectively.

A comparison between the different pump fluences excited at 3.1 eV shows only a small difference in the amplitude despite the factor 4 in the excitation intensity. Note that the pump fluences of 140 µJ/cm² and 35 µJ/cm² were measured at two different positions of the sample. By the inhomogeneous spatial distribution of the NWs, it is likely that the number of NWs in the pump and probe spot varied between these two measurements. In general, for experiments on the same sample spot, we observe a linear scaling of the peak value of the transient signal with the pump fluence.
References

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