Supporting Information

Harnessing the interplay between photonic resonances and carrier extraction for narrowband germanium nanowire photodetectors spanning the visible to infrared

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A. Fabrication scheme

Key steps in the fabrication process are shown in Fig. S1 below. These are also described in the main manuscript.

Figure S1. Fabrication process for Ge NW photodetectors.
B. Characterization of Ge growth stack

We perform secondary ion mass spectroscopy (SIMS) of the Ge wafer after epitaxial growth of the n+ and intrinsic (unintentionally doped) layers. The result is shown in Fig. S2. The etched NW height (2 μm) is also indicated on this graph.

Figure S2. SIMS of Ge growth stack on p+ Ge substrate.
C. Light absorption in vertical nanowires

As discussed in our previous work\textsuperscript{1}, the phenomenon of spectrally selective absorption in NWs arises from the wavelength-dependence of the field distribution of the fundamental (or higher order) guided mode of the NW. In particular, it comes about from the interplay between coupling efficiency and absorption in the NW\textsuperscript{1}. In Seo et. al., we considered the case of a 90 nm diameter Si NW. It was noted that, at short wavelengths (e.g. $\lambda = 400 \text{ nm}$), the field distribution of the fundamental guided mode is such that the fields are highly confined to the core. This results in the coupling efficiency from free-space plane wave illumination being very low, due to very small mode overlap. It was similarly noted that, at long wavelengths (e.g. $\lambda = 650 \text{ nm}$), the field distribution of the fundamental guided mode is such that the fields are largely expelled from the core. The coupling efficiency (from free-space illumination) is high. However, it was noted that the fields within the NW are small, and therefore the absorption is small. We observed that, at intermediate wavelengths (e.g. $\lambda = 547 \text{ nm}$), the field distribution extends over a distance from the NW that is large enough to make the coupling relatively efficient. Furthermore, the fields within the NW are large, making the absorption appreciable. At these intermediate wavelengths, therefore, the absorption spectra exhibit peaks. In our earlier work\textsuperscript{1}, this phenomenon was studied by plotting the field distribution of the fundamental guided mode in Si NWs. In Fig. S3, we plot the field distributions for the fundamental guided mode in Ge NWs with diameters of 150 nm and 250 nm at a few representative wavelengths. These are found using a commercial software package that solves for waveguide modes (Mode Solutions, Lumerical). For the 150 nm diameter NW, it can be seen that for a wavelength of $\lambda = 975 \text{ nm}$, the mode has an appreciable extent (spreading into the air surrounding the NW) while the field inside the NW is large. This is also the case for the 250 nm diameter NW, at wavelength
\( \lambda = 1450 \text{ nm} \). As we will see later, at these wavelengths, the NWs exhibit peaks in their absorption spectra. This confirms that our physical interpretation developed for Si NWs, also applies to the Ge NWs considered in this study.

Figure S3. Major transverse component of the electric field (\( E_x \)) for fundamental mode (\( HE_{11} \)) of the NW at various wavelengths. Upper plots: NW diameter is 150 nm. Lower panels: NW diameter is 250 nm.

We next consider the absorption efficiencies of square arrays of Ge NWs (period 1 \( \mu m \)). To facilitate physical interpretation, we consider the simple case of NWs with uniform circular cross sections (i.e. non-tapered) in air. The NWs have heights of 2 \( \mu m \). In Fig. S4a, the simulated absorption efficiency is plotted as a function of diameter and wavelength. Bands of high absorption associated with the \( HE_{11} \) and \( HE_{12} \) modes can be seen. It is notable that the high absorption peak associated with the \( HE_{11} \) mode can be tuned from visible (600 nm) to SWIR (1600 nm) wavelengths. Features at wavelengths around 1000 nm can also be seen, and are associated with a diffraction mode in the plane of the array (i.e. perpendicular to NW axis). In Fig. S4b, the simulated absorption spectrum of an array of NWs with diameters of 200 nm is shown. In Fig S4c and S4d, we plot intensity distributions for the NW (200 nm diameter) for
illumination at $\lambda = 1200\, nm$ and $\lambda = 1000\, nm$, respectively. These patterns confirm our identification of the spectral features at these wavelengths being associated with the $HE_{11}$ and grating modes, respectively.

Figure S4. (a) Absorption efficiency of square arrays of Ge NWs (height 2 $\mu$m) in air, as a function of diameter and wavelength. (b) Absorption efficiency vs. wavelength for a square array of Ge NWs with diameters of 200 nm. Intensity ($|E|^2$) vs. position along a cross-section through 200 nm diameter NW, for illumination at (c) $\lambda = 1200\, nm$ and at (d). $\lambda = 1000\, nm$. 
D. Ideality factor from I-V plots

The current across a p-n junction with a series resistance and shunt resistance in forward bias is given by:

\[
I = I_0 \left[ \exp \left( \frac{q(V - IR_s)}{n k_B T} \right) - 1 \right] + \frac{V - IR_s}{R_{sh}}
\]

where, \(q\) is the electronic charge, \(V\) the voltage applied across the diode, \(k_B\) is Boltzmann’s constant, \(T\) the absolute temperature, \(n\) is the ideality factor, \(I_0\) is the reverse saturation current, \(R_s\) is the series resistance and \(R_{sh}\) is the shunt resistance (Fig. S5a). We use non-linear regression to determine the values of \(I_0, n, R_s\) and \(R_{sh}\) that gives the best agreement between the above equation and the measured I-V characteristics under forward bias.

![Diagram](image)

**Figure S5.** Fitting of diode parameters (a) Equivalent circuit diagram of the diode with series and shunt resistance in forward bias (b) I-V characteristics: measured (red dots) and model (black line) with values of \(I_0, n, R_s\) and \(R_{sh}\) as indicated.

The results are shown in Fig. S5b. The best fit gives series and shunt resistances of 27.3 ohms and \(5 \times 10^5\) ohms, respectively. The diode shows high reverse saturation current of \(\sim 1.12 \times\)
$10^{-4}$ A, suggesting substantial leakage. It should be further noted that high leakage is anticipated for Ge devices owing to the small bandgap and low ionization energy of Ge when compared to Si. The ideality factor is found to be $\sim 4$. This can be attributed to large p-i-n junction edge area in our NW diode arrays which leads to increased trap-assisted surface recombination. The fact that $n > 2$ suggests that our diode does not perform in the ideal regime and that other recombination processes such as trap assisted tunnelling and field enhanced recombination dominate$^2$. 
E. Model for calculating carrier collection probability

Details on the setup of electrical simulations (transport part):

We assume that the mobility of the germanium of our NWs is that of crystalline germanium. We also assume that the fact that the devices are NWs with diameters down to 75 nm, rather than bulk structures, has a negligible impact on the electrical properties of the materials. We assume that all dopants are activated and that the homojunction interfaces are perfect. As both ends of the NW devices are highly doped (degenerate), we assume that there is negligible recombination at the interfaces between these regions and the metal contacts. We, therefore, assume that these contacts are Ohmic. Recombination mechanisms that might occur in the NWs include Shockley-Read-Hall (SRH) recombination in the NW bulk, Auger recombination, and surface recombination (SRH recombination through surface states) and they are all included in the simulation. Auger recombination factors of both holes and electrons are assumed to be 1E-31 cm$^6$s$^{-1}$ from Ref [3]. The electron and hole lifetime for SRH recombination are assumed to be 40 microseconds$^4$. We find that the rate of Auger recombination is several orders of magnitude lower than that of surface recombination in the intrinsic region of our NW, in which the majority of the optical absorption takes place. Our reasoning is based on Ref [5]. Detailed mathematical models for the recombination mechanisms are described in Refs [4,6].

The simulation performed is in steady-state. The main equations for the simulation are as follows:

a) Poisson equation. $\nabla \cdot (\varepsilon E) = q\left(p - n + N_D^+ - N_A^-\right)$

b) Both types of carriers are considered. The carriers satisfy the steady-state continuity equations:
\[ \nabla \cdot J_p = e(R_p - G_p) \] for holes

\[ \nabla \cdot J_n = -e(R_n - G_n) \] for electrons.

c) Both drift and diffusion are considered:

\[ J_p = pe\mu_p E + \mu_p k_B T \nabla p \] for holes

\[ J_n = ne\mu_n E - \mu_n k_B T \nabla n \] for electrons.

The electrical simulation is computationally demanding due to the existence of multiple transport mechanisms and complicated boundary conditions. Rather than performing a full three-dimensional simulation, we make the simplifying assumption that variation with the polar angle can be neglected. This appropriate due to the symmetry of our structure, and the fact that the rate of photogeneration of carriers is small enough for this process to be considered perturbative. This allows us to perform the modelling in two dimensions. The modelled structure is a tapered Ge NW, comprising a cylinder whose top and bottom diameters are chosen to match the dimensions of the actual devices (as found from SEM images). The doping profile is modelled to match the doping profile determined by the SIMS measurement. The top section of the NW is doped n+ and is 300 nm thick. A doping density varying linearly from 3E+19 cm\(^{-3}\) (tip) to 1E+19 cm\(^{-3}\) (300 nm below the tip) is assumed. The intrinsic region (below it) is 1500 nm thick. The bottom section of the NW is doped p+ and is 200 nm thick. A doping density of 5E+18 cm\(^{-3}\) is assumed. To model the application of a voltage across the device, we set the difference between the potentials applied to the top and bottom of the NW. These applied potentials are taken as being uniform on the circular cross section of the NW.
Our chief goal in performing the electrical modelling is to determine internal quantum efficiency (IQE) as a function of position in the NW. To do so, we impose a uniform electron-hole pair generation rate \( G_n = G_p \) over an annulus that has a height of 30 nm (along the NW axis) and a width of 8 nm (along the radial direction). We then find the rate of carrier collection at the ends of the NW by numerical solution (in the COMSOL Multiphysics package) of the equations discussed above. In this way, the IQE is found for a particular annulus position. This process is repeated with different annulus positions to generate a spatial map of the IQE over the NW. As discussed in the main manuscript, surface recombination (occurring at the Al\(_2\)O\(_3\)-Ge interface) is of critical importance in our devices. Ideally, we would experimentally determine the precise energies and densities of the surface states, and use these in the modelling. This is beyond the scope of this work, however, and we instead model surface recombination using the two energy states near the midgap that were reported in Refs [7,8] for the interface between germanium and aluminium oxide. These states have energies of 0.194 eV from valence band top and 0.152 eV from conduction band bottom, respectively. The values we use for the electron and hole capture cross-sections are \( 2 \times 10^{-14} \text{cm}^2 \) and \( 6.7 \times 10^{-16} \text{cm}^2 \), respectively. These are taken from Ref [9]. These values pertain to Ge surfaces, rather than to the Al\(_2\)O\(_3\)-Ge interface. As discussed above, one would ideally measure these for the Al\(_2\)O\(_3\)-Ge interface, but this is beyond the scope of this work. We use \( 1 \times 10^7 \text{cm/s} \) as the thermal velocity of both electrons and holes.

**Carrier collection probabilities in different parts of the nanowire: physical interpretation**

As discussed above and in the main manuscript, the predicted EQE at each wavelength is found by simulating the optical absorption as a function of position in the NW device by the FDTD method. This is converted to generation rate by assuming that each absorbed photon creates an
exciton. We then multiply the generation rate by the carrier collection probability and integrate over the NW to find the EQE. The carrier collection probability is thus of key importance in determining the EQE. We provide a physical interpretation of the carrier collection probabilities in the different regions of the NW below.

In the depletion regions, high built-in electric fields facilitate the excitons being split and quickly swept to the two sides of the junction, for collection by the heavily doped electrodes. The carriers can thus be collected before surface recombination occurs, and the carrier collection efficiencies in these regions are high. We next consider the neutral (intrinsic) region between the depletion regions. As seen in the band diagram of Fig. S6, the electric field here is approximately zero. Carrier transport is mainly by diffusion, and carrier collection is therefore much less efficient as the process is slow and is impacted by surface recombination. Indeed, one could obtain a reasonable estimate of the EQE vs. wavelength curve by only integrating the light absorbed in the depletion regions.
Figure S6. Electrical modelling of NW by COMSOL Multiphysics package. Top: electric field as a function of distance along the centre of NW. Middle: electric potential on a cross-section through NW. Bottom: electric potential as a function of distance along the centre of NW. Simulations are performed with zero applied bias, for NW with top and bottom diameters of 125 and 164 nm, with an assumed surface trap density of 5E+13 cm$^{-2}$.
F. Collection probability vs. surface trap density

In the figure below, we plot the simulated carrier collection probability over a cross section of the NW, for different choices of surface trap density. A significant drop in the peak value of the carrier collection probability, and the spatial extent of the collection region can be seen as the surface trap density is increased from $1E+12$ cm$^{-2}$ to $5E+13$ cm$^{-2}$.

Figure S7. Carrier collection probability plotted on an $x - z$ cross-section through a tapered NW with a nominal diameter of 75 nm.
G. Simulated absorption efficiency vs. wavelength for nanowires of various diameters

In Fig. 3c of the main manuscript, simulated absorption spectra of a selection of NW devices are provided. In Fig. S8 (below), we provide the simulated absorption spectra of NWs with all diameters studied in this work. In simulations, nanowires are tapered, with different top and base diameters that match those of actual devices (as found from SEM images). As before, nominal diameters represent the design values chosen in the e-beam lithography step. A table of tip, base and nominal diameters for different devices is provided below.

<table>
<thead>
<tr>
<th>NW Array</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tip Diameter(nm)</td>
<td>75</td>
<td>100</td>
<td>125</td>
<td>150</td>
<td>175</td>
<td>200</td>
<td>225</td>
<td>250</td>
</tr>
<tr>
<td>Base Diameter(nm)</td>
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<td>135</td>
<td>164</td>
<td>187</td>
<td>208</td>
<td>230</td>
<td>262</td>
<td>290</td>
</tr>
<tr>
<td>Nominal Diameter (nm)</td>
<td>75</td>
<td>100</td>
<td>125</td>
<td>150</td>
<td>175</td>
<td>200</td>
<td>225</td>
<td>250</td>
</tr>
</tbody>
</table>

The simulations below incorporate all layers used in the fabrication of actual devices (e.g. ITO, Au, PMMA, Al2O3, etc.).
Figure S8. Simulated absorption efficiency vs. wavelength for different diameter nanowires.
H. Complete set of calculated EQE data

In Fig. 3d and Fig. 5 of the main manuscript, simulations of EQE wavelength are provided for a selection of NW diameters and trap densities. In Fig. S9, we present the complete set of calculated EQE vs. wavelength spectra for all studied diameters and trap densities. Due to a large number of plots, in this figure, panels a-d are shown on separate pages. Panels a-d present EQE spectra for trap densities of $S = 1E + 12 \, cm^{-2}$, $S = 5E + 12 \, cm^{-2}$, $S = 1E + 13 \, cm^{-2}$, and $S = 5E + 13 \, cm^{-2}$, respectively.
**Figure S9a.** Simulated EQE with surface trap density $S = 1\times10^{12}$ cm$^{-2}$. 
Figure S9b. Simulated EQE with surface trap density $S = 5E+12 \text{ cm}^{-2}$. 
Figure S9c. Simulated EQE with surface trap density $S = 1E+13 \, \text{cm}^{-2}$.
Figure S9d. Simulated EQE with surface trap density $S = 5E+13 \text{ cm}^{-2}$. 
Supporting References


(9) Many, A.; and Gerlich, D. Distribution and Cross Sections of Fast States on Germanium Surfaces in Different Gaseous Ambients. Phys. Rev. 1957, 107, 404