Radial modulation doping in core–shell nanowires

David C. Dillen, Kyoungwan Kim, En-Shao Liu and Emanuel Tutuc*

Semiconductor nanowires are potential candidates for applications in quantum information processing\textsuperscript{3,4}, Josephson junctions\textsuperscript{6,8} and field-effect transistors\textsuperscript{5,9} and provide a unique test bed for low-dimensional physical phenomena\textsuperscript{7}. The ability to fabricate nanowire heterostructures with atomically flat, defect-free interfaces enables energy band engineering in both axial\textsuperscript{10-12} and radial\textsuperscript{13-16} directions. The design of radial, or core–shell, nanowire heterostructures relies on energy band offsets and strain. The charge-transfer and confinement mechanism can be used to achieve modulation doping\textsuperscript{17,19} in core–shell structures\textsuperscript{20,21}. By selectively doping the shell, which has a larger bandgap, charge carriers are donated and confined in the core, generating a quasi-one-dimensional electron system with higher mobility. Here, we demonstrate radial modulation doping in coherently strained Ge–Si\textsubscript{x}Ge\textsubscript{1-x} core–shell nanowires and a technique to directly measure their valence band offset. Radial modulation doping is achieved by incorporating a B-doped layer during epitaxial shell growth. In contrast to previous work showing site-selective doping in Ge–Si core–shell nanowires\textsuperscript{21,22}, we find both an enhancement in peak hole mobility compared with undoped nanowires and observe a decoupling of electronic transport in the core and shell regions. This decoupling stems from the higher carrier mobility in the core than in the shell and allows a direct measurement of the valence band offset for nanowires of various shell compositions.

Our modulation doped Ge–Si\textsubscript{1-x}Ge\textsubscript{x} core–shell nanowires were grown using a two-step process. First, Ge nanowire cores were grown using an Au-catalysed vapour–liquid–solid (VLS) mechanism, using GeH\textsubscript{4} as precursor. Following the Ge nanowire growth, an epitaxial Si\textsubscript{1-x}Ge\textsubscript{x} shell was grown in situ by ultrahigh-vacuum (UHV) chemical vapour deposition (CVD) using a combination of SiH\textsubscript{4} and GeH\textsubscript{4} as precursors (see Methods). Two types of radial nanowire heterostructure were grown and investigated. In the first heterostructure type, the Si\textsubscript{1-x}Ge\textsubscript{x} shell was grown undoped. In the second, we combined modulation doping using B as acceptor with the epitaxial Si\textsubscript{1-x}Ge\textsubscript{x} shell growth. Specifically, during Si\textsubscript{1-x}Ge\textsubscript{x} shell growth, B\textsubscript{2}H\textsubscript{6} (100 ppm in He) was introduced for 6 min at the mid-point of the 60 min shell growth. Figure 1a presents a schematic representation of modulation-doped core–shell nanowire growth.

For both types of heterostructure, undoped or modulation-doped, we grew Ge–Si\textsubscript{1-x}Ge\textsubscript{x} core–shell nanowires with different relative Si/Ge content in the shell by tuning the GeH\textsubscript{4} to SiH\textsubscript{4} gas flow ratios during shell growth\textsuperscript{23}. Table 1 summarizes the shell thickness (t\textsubscript{s}) and relative Si content (\chi), determined by transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy, for all the heterostructures investigated. The TEM micrograph in Fig. 1b demonstrates the single-crystal structure of the modulation-doped Ge–Si\textsubscript{1-x}Ge\textsubscript{x} core–shell nanowire (sample C in Table 1), together with the expected dopant position.

The epitaxial quality of the core–shell interface was further revealed by the Raman spectra of Fig. 1c, which show a shift of the core–shell nanowire’s Ge–Ge mode to higher frequencies compared with the bare Ge nanowire mode at 300.5 cm\textsuperscript{-1}. This blueshift is attributed to a compressive strain in the Ge core due to mismatch of the equilibrium lattice constant at the core–shell interface\textsuperscript{24,25} and is present along the entire length of the nanowire. A comparison of Raman mode frequencies with lattice dynamical theory calculations combined with a continuum elasticity strain model\textsuperscript{25} show very good agreement, indicating little or no strain relaxation and a nominally defect-free core–shell interface in our samples.

To probe the electrical characteristics of the nanowire heterostructures, we fabricated Ge–Si\textsubscript{1-x}Ge\textsubscript{x} core–shell nanowire field-effect transistors (FETs) with an Ω-shaped gate geometry and gate lengths \(L_\text{g}\) between 250 and 1,500 nm (see Methods). Low-resistance, ohmic contacts were realized by ion implantation with B (ref. 26), allowing for extraction of the intrinsic transport properties of the nanowire. A scanning electron micrograph example of a completed device is shown in Fig. 2a, together with a schematic of the device structure.

We measured the electrical characteristics of each device at temperatures between 77 K and 300 K by probing both the drain current versus drain voltage (\(I_\text{d}–V_\text{d}\)) at fixed gate bias \(V_\text{g}\), and \(I_\text{d}–V_\text{g}\) at fixed \(V_\text{d}\). Figure 2b,c shows the \(I_\text{d}–V_\text{d}\) and \(I_\text{d}–V_\text{g}\) characteristics, respectively, of a modulation-doped Ge–Si\textsubscript{0.45}Ge\textsubscript{0.55} core–shell nanowire (sample B) with channel length \(L_\text{g} = 1,050\) nm and diameter \(d = 43\) nm. The positive threshold voltage and increasing \(I_\text{d}\) with decreasing \(V_\text{g}\) indicate p-type depletion mode operation in the modulation-doped nanowires. We found that the modulation-doped Ge–Si\textsubscript{0.45}Ge\textsubscript{0.55} core–shell nanowires have a peak mobility \(\mu = 700–1,800\) cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} at 77 K (see Methods), whereas the non-modulation-doped nanowires with similar shell content show a peak \(\mu = 100–280\) cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} at 77 K. The increase in mobility thanks to the modulation doping is similar to the mobility enhancement observed in planar, group IV-based modulation-doped field-effect transistors (MODFETs)\textsuperscript{27}.

Figure 3a presents a comparison of the conductivity \(G\) measured at 77 K as a function of \(V_\text{g}\) in two Ge–Si\textsubscript{0.45}Ge\textsubscript{0.55} core–shell nanowires, one nominally undoped and one modulation-doped. Figure 3a reveals two findings. First, the threshold voltage of the modulation-doped nanowire is shifted to a more positive value, consistent with p-type doping. More importantly, the \(G–V_\text{g}\) data show a clear slope change at \(V_\text{g} = 0.81\) V, corresponding to a gate overdrive of \(\Delta V_\text{g} = 0.44\) V. This peculiar feature is consistently present in the modulation-doped Ge–Si\textsubscript{0.45}Ge\textsubscript{0.55} nanowires investigated in our study. In contrast, undoped Ge–Si\textsubscript{0.45}Ge\textsubscript{0.55} core–shell nanowires show an almost linear \(G–V_\text{g}\) dependence, without noticeable features, a finding also consistent with previous reports\textsuperscript{8,16}.

To further illuminate the source of the kink in Fig. 3a, we performed finite-element calculations of the hole density \(p\) versus \(V_\text{g}\), and \(I_\text{d}–V_\text{g}\) for modulation-doped Ge–Si\textsubscript{0.45}Ge\textsubscript{0.55} core–shell nanowires.
core–shell nanowires showing the VLS growth (green) and CVD SiGe shell growth (blue) with B modulation-doped region (red). Arrows indicate the growth direction in each regime.

**Figure 1** | Nanowire growth and structural characterization. a, Growth schematic for modulation-doped Ge-SiGe core–shell nanowires showing Ge core growth (green) and CVD SiGe shell growth (blue) with B modulation-doped region (red). Arrows indicate the growth direction in each regime. b, TEM image and EDX linescan data (inset) from a Ge-Si$_{0.45}$Ge$_{0.55}$ core–shell nanowire. Yellow lines delineate the shell region, and the red dashed line marks the expected position of B dopants. EDX data fitting indicates a Si$_{0.63}$Ge$_{0.37}$ shell thickness of 3.0 nm. c, Raman spectra showing the core Ge–Ge mode from a Ge nanowire (black), and Ge-Si$_{0.45}$Ge$_{0.55}$ (red) and Ge-Si$_{0.45}$Ge$_{0.57}$ (green) core–shell nanowires, each of 50 nm diameter. The blueshift of the core–shell spectra indicates a compressively strained core.

**Table 1** | Core–shell nanowire growth parameters and measured shell thickness/composition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulation doping</th>
<th>GeH$_4$/SiH$_4$ flow during shell growth (s.c.c.m.)</th>
<th>Shell material</th>
<th>Shell thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>No</td>
<td>10/50</td>
<td>Si$<em>{0.46}$Ge$</em>{0.54}$</td>
<td>5.2</td>
</tr>
<tr>
<td>B</td>
<td>Yes</td>
<td>10/50</td>
<td>Si$<em>{0.46}$Ge$</em>{0.55}$</td>
<td>5.0</td>
</tr>
<tr>
<td>C</td>
<td>Yes</td>
<td>5/50</td>
<td>Si$<em>{0.63}$Ge$</em>{0.37}$</td>
<td>3.0</td>
</tr>
</tbody>
</table>

See Methods for further details about the growth process.

(see Methods). Figure 3b shows $p$ versus $V_g$ in both the core and shell regions. At large positive $V_g$, both the core and shell are fully depleted of carriers. As $V_g$ is decreased to 1.1 V, holes begin to populate the core first, thanks to the positive valence band offset, $\Delta E_p = E_{Vb,Ge} - E_{Vb,Ge,core}$. Further decreasing $V_g$ to negative values will induce holes in the shell, accompanied by saturation of the core’s hole density as a function of $V_g$ (Fig. 3b). A radial slice of the valence band energy (black line) and $p$ (red line) under these biasing conditions is shown in Fig. 3c. Hole density calculations were also performed for Ge–Si$_x$Ge$_{1-x}$ core–shell nanowires without modulation doping (Supplementary Fig. 1). These results are qualitatively similar to the Fig. 3b data, except for a negative shift in the voltage required to populate both core and shell regions, together with a slight decrease in the saturation level of the core hole density. The $V_g$ value at the onset of shell hole occupation is evident in the $I_g$–$V_g$ calculations of Fig. 3d, which show a kink in the slope of the $I_g$–$V_g$ curve at the same $V_g$. As we show in Fig. 3d, the kink position ($V_{g,kink}$) depends on the core-to-shell band offset and shifts to higher $V_g$ as the defined $\Delta E_p$ is decreased.

The combination of experimental data and finite-element calculations strongly suggests that the kink observed in the $G$–$V_g$ data of modulation-doped Ge–Si$_x$Ge$_{1-x}$ core–shell nanowires marks the onset of the shell being populated with carriers at high gate overdrive and stems from a larger carrier scattering rate in the shell due to fixed charge impurities. At low gate overdrive, the carriers are confined to the Ge core and the ionized acceptor impurity scattering rate is low. By populating the shell, we effectively decrease the hole mobility due to additional ionized impurity scattering, resulting in an abrupt decline of the slope of the $I_g$–$V_g$ data. In a heterostructure with small $\Delta E_p$, the core hole density saturation and shell population occur at a relatively low gate overdrive, resulting in a small $|V_{th} - V_{kink}|$. As $\Delta E_p$ increases, the onset of shell population...
For two different values of core–shell nanowire at 77 K. A clear kink, marked with an arrow, is observed for the modulation-doped nanowires. The data for

\begin{align*}
\text{NA TURE NANOTECHNOLOGY} & \\
\text{experimentally measured for an undoped and a} & \\
\text{modulation-doped nanowire heterostructure, assuming} & \\
\text{\( \Delta E_v = 400 \text{ meV} \)} & \\
\text{value an} & \\
\text{and a cubic Ge} & \\
\text{| 40 nm. Thanks to the} & \\
\text{core–shell nanowires should have a large Si shell} & \\
\text{order 130 meV over} & \\
\text{10} & \\
\text{5.0 nm,} & \\
\text{data at all values of} & \\
\text{versus} & \\
\text{values for two different} & \\
\text{data from modulation-doped Ge–Si} & \\
\text{values and with shell thickness, Al} & \\
\text{O} & \\
\text{due to an uncertainty in shell thickness of} & \\
\text{0.45, increasing to 270 meV (six devices) at} & \\
\text{core–shell nanowire} & \\
\text{t} & \\
\text{×} & \\
\text{I} & \\
\text{5} & \\
\text{data (Fig. 3a) and finite-element} & \\
\text{processing variations, such as variations in oxide thickness or} & \\
\text{dielectric constant, and errors in determining the experimental} & \\
\text{V} & \\
\text{| V} & \\
\text{Kink} & \\
\text{value. For comparison, in Fig. 4b we plot the} & \\
\text{data for two different} & \\
\text{planar Si_{Ge} – Ge heterostructures. The solid line depicts} & \\
\text{core-level electron energy loss spectroscopic (EELS) measurements} & \\
\text{of \( \Delta E_v \) at an unstrained Si_{Ge} – Ge interface\textsuperscript{38}, while the dashed} & \\
\text{line corresponds to \( \Delta E_v \) between strained Si_{Ge} and a cubic Ge} & \\
\text{substrate, calculated using an empirical pseudopotential method\textsuperscript{39}.} & \\
\text{Although the strain distribution in the core–shell nanowire is} & \\
\text{expected to be more complicated than that of the planar structure\textsuperscript{30–32}, our} & \\
\text{data for modulation-doped Ge–Si_{Ge} core–shell nanowires match relatively well with calculations for} & \\
\text{the strained planar structure (dashed line). The unstrained curve (solid line) overestimates our \( \Delta E_v \) at all values of} & \\
\text{Based on these results and those of previous works, high-mobility Ge–Si_{Ge} core–shell nanowires should have a large Si shell composition (\( x \)) to maximize the valence band confinement energy and hole mobility\textsuperscript{40}, while also reducing the interface trap}
\end{align*}

Figure 3 | Decoupled core and shell transport in modulation-doped nanowires. a. Comparison of G–V\textsubscript{g} experimentally measured for an undoped and a modulation-doped Ge-Si\textsubscript{0.45}Ge\textsubscript{0.55} core–shell nanowire at 77 K. A clear kink, marked with an arrow, is observed for the modulation-doped nanowires. The dashed lines are guides to the eye to help identify the kink position. b. Core (black), shell (red) and total (green) hole densities per unit length calculated as a function of V\textsubscript{g} for the modulation-doped nanowire heterostructure, assuming \( \Delta E_v = 400 \text{ meV} \). The dotted line designates the threshold for hole population of the shell. c. Radial dependence of the valence band edge (black) and hole density (red) for the modulation-doped nanowire at two different V\textsubscript{g}. Dashed lines indicate the Fermi energy. d. Calculated I\textsubscript{d}–V\textsubscript{g} data for the same heterostructure as in a–c for two different values of \( \Delta E_v \). The dotted line marks the kink in I\textsubscript{d}–V\textsubscript{g} for \( \Delta E_v = 400 \text{ meV} \).
in situ onto the Ge core using UHV chemical vapour deposition at \( \sim 380 \) °C, with GeH4 (20.8% in He, 5 or 10 s.c.c.m.) and SiH4 (50%, 50 s.c.c.m.) precursors, at a total chamber pressure of 40 mtorr. Boron modulation doping was incorporated into the shell growth by the addition of \( \text{B}_2\text{H}_6 \) (100 ppm in He, 50 s.c.c.m.) to the gas ambient. To gate dielectrics. \( \equiv \) \( \frac{1}{2} \) \( \pm \) (20.8% in He, 50 s.c.c.m.) precursor at 2.5 torr. Because of the \( R_{12} \), \( 195314 \) (2011). as a function of \( is used to extract the core-to-shell valence band offset. \( R_{19} \), the gate top was defined using electron-beam lithography, sputtered tantalum nitride (TaN) and lift-off in acetone. The \( \text{Al}_2\text{O}_3 \) film was then etched from the source and drain regions in dilute HF acid. To realize a low extrinsic series resistance in these devices, the samples were B-implanted at an energy of \( 3 \) keV and a dose of \( 1 \times 10^{13} \) cm\(^{-2} \), using the TaN gate as the implant mask. Devices were activated in a rapid thermal annealing furnace at \( 500 \) °C for \( 5 \) min in \( N_2 \) ambient. To complete device fabrication, \( 80-\) nm-thick Ni source–drain contacts were defined by electron-beam lithography, electron-beam evaporation and lift-off in acetone.

**Fabrication of nanowire FETs.** Nanowires were removed from the growth substrate by sonication in ethanol, followed by dispersal on a \( 54 \) nm \( \text{SiO}_2 \) substrate, which can also serve as the backgate. We then grew an \( 8-\) nm-thick \( \text{Al}_2\text{O}_3 \) top-gate dielectric using atomic layer deposition, which yielded conformal film growth. The top gate was defined using electron-beam lithography, sputtered tantalum nitride (TaN) and lift-off in acetone. The \( \text{Al}_2\text{O}_3 \) film was then etched from the source and drain regions in dilute HF acid. To realize a low extrinsic series resistance in these devices, the samples were B-implanted at an energy of \( 3 \) keV and a dose of \( 1 \times 10^{13} \) cm\(^{-2} \), using the TaN gate as the implant mask. Devices were activated in a rapid thermal annealing furnace at \( 500 \) °C for \( 5 \) min in \( N_2 \) ambient. To complete device fabrication, \( 80-\) nm-thick Ni source–drain contacts were defined by electron-beam lithography, electron-beam evaporation and lift-off in acetone.

**Nanowire mobility extraction.** The measured resistance \( R_m \) of the nanowire FET is the sum of the intrinsic nanowire channel resistance \( R_m \), the contact resistance \( R_c \) and the ungated source–drain extension resistance \( R_{ext} \). The nanowire resistivity and \( R_c \) values of \( \pm 0.4 \) m\( \Omega \) cm and \( 300 \pm 200 \) \( \Omega \) \( \Omega \), respectively, were determined using data from B-implanted nanowires\(^{33} \). The external series resistance \( R_{ext} \) of the devices probed in this work was \( 15.8 \pm 2.3 \) k\( \Omega \). We determined \( \mu \) as a function of \( V_g \) using \( \mu = \frac{I_g}{V_g} \), where \( R_m = R_{ext} - (R_c + R_m) \) and \( p(V_g) \) is the hole density per unit length as determined by finite-element calculation.

**Finite-element calculations of hole density and transport.** The hole density was obtained through a finite-element calculation (Sentaurus, Synopsys) using a full quantum-mechanical solution based on a density gradient model, with the modulation doping density set to \( \sim 10^{10} \) cm\(^{-2} \) over a thickness of \( 1.0 \) nm and assuming a temperature of \( 77 \) K. A gate-all-around structure was used in place of the actual \( \Omega \)–shaped gate for computational efficiency, although the results obtained using both structures were identical. For transport calculations, we used a constant mobility model with explicitly defined core and shell values of \( 1.900 \) and \( 450 \) cm\(^2\) V\(^{-1}\) s\(^{-1} \), respectively. These values were chosen only to be comparable to experimental values, not to exactly match experimental \( I_g-V_g \) data. It should be noted that the actual mobilities used in simulation are inconsequential, as \( V_{th} \), the parameter of interest in this study, was found to be constant over large changes in mobility. We must, however, choose mobilities such that \( \mu_{core} \equiv \mu_{shell} \) in order to observe a kink in simulated \( I_g-V_g \) curves, a situation activated experimentally with the addition of modulation doping.

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**References**


**Methods**

**Ge–SiGe\(_{1-x}\) core–shell nanowire growth and structure characterization.** A 7-Å-thick Au layer was evaporated onto a Si(111) wafer following removal of native oxide in dilute hydrofluoric (HF) acid. The wafer was then transferred to the cold-wall UHV growth chamber and annealed for 15 min in H\(_2\) ambient at \( \sim 370 \) °C to produce Au nanoparticles, which act as a catalyst for nanowire growth. The Ge nanowire core was grown using the VLS process at a substrate temperature of \( \sim 280 \) °C using GeH\(_4\) (20.8% in He, 50 s.c.c.m.) precursor at 2.5 torr. Because of the finite radial Ge growth rate during VLS core growth, we see a slight tapering of the Ge core diameter from base to tip. The Si\(_{1-x}\) Ge\(_x\) shell was then grown epitaxially

**Figure 4 | Valence band offset extraction.** a. Calculated \( |V_m-V_{th}| \) versus \( \Delta V \) for a 40-nm-diameter modulation-doped Ge–Si\(_{1-x}\)Ge\(_x\) core–shell nanowire, with \( V_m = 5.0 \) nm and \( \text{Al}_2\text{O}_3 \) thickness \( t_{Al_2O_3} = 8.35 \) nm. Filled symbols represent calculations with \( D_{Al_2O_3} = 0 \), and open symbols correspond to \( D_{Al_2O_3} = 5 \times 10^{12} \) cm\(^{-2}\) eV\(^{-1}\). b. \( \Delta V \) extracted from experimental \( |V_m-V_{th}| \) values of modulation-doped Ge–Si\(_{1-x}\)Ge\(_x\) core–shell nanowires at 77 K assuming both \( D_{Al_2O_3} = 0 \) (filled symbols) and \( D_{Al_2O_3} = 5 \times 10^{12} \) cm\(^{-2}\) eV\(^{-1}\) (open symbols). The solid line represents previously measured \( \Delta V \) values in unstrained planar Ge–Si\(_{1-x}\)Ge\(_x\) interfaces\(^{28} \), while the dashed lines are calculated \( \Delta V \) values in strained Si\(_{1-x}\)Ge\(_x\) on cubic Ge (ref. 29).


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Author contributions

D.C.D. performed nanowire sample growth, nanowire device fabrication and characterization, with assistance from K.K. and E-S.L. D.C.D. and E.T. analysed the data and wrote the paper, with input from all authors.

Additional information

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Competing financial interests

The authors declare no competing financial interests.