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Single crystalline kinked semiconductor nanowire superstructures

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Abstract

The ability to control and modulate the composition^{1–4}, doping^{1,3–5}, crystal structure^{6–8} and morphology^{9,10} of semiconductor nanowires during the synthesis process has allowed researchers to explore various applications of nanowires^{11–15}. However, despite advances in nanowire synthesis, progress towards the *ab initio* design and growth of hierarchical nanostructures has been limited. Here we demonstrate a ‘nanotectonic’ approach that provides iterative control over the nucleation and growth of nanowires and use it to grow kinked or zigzag nanowires in which the straight sections are separated by triangular joints. Moreover, the lengths of the straight sections can be controlled and the growth direction remains coherent along the nanowire. We also grow dopant-modulated structures in which specific device functions, including p-n diodes and field-effect transistors, can be precisely localized at the kinked junctions in the nanowires.

We have focused on rational design and synthesis of two dimensional (2D) multiply-kinked nanowires (Fig. 1a), where kinks are introduced at defined positions during growth and are confined to a single plane. These hierarchical nanowires are built-up using a ‘nanotectonic’ approach analogous to metal-organic framework materials¹⁶, where we define a ‘secondary building unit’ (SBU)¹⁶ consisting of two straight single-crystalline arms (blue, Fig. 1a) connected by one fixed 120° angle joint (green, Fig. 1a). We note that two $\langle 112 \rangle_c$ or $\langle 110 \rangle_c$ vectors in a cubic crystal structure, and two $\langle 11-20 \rangle_h$ or $\langle 1-100 \rangle_h$ vectors in a hexagonal structure can form the desired 120° joint when rotating about the $\langle 111 \rangle_c$ and $\langle 0001 \rangle_h$ zone axes, respectively (Fig. 1a; Supplementary Fig. S1). SBU formation involves three main steps during nanocluster-catalyzed growth (Fig. 1b); (A) axial growth of a 1D

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Author Contributions

B.T. and C.M.L. designed the experiments. B.T., P.X. and T.J.K. performed experiments and analyses. B.T. and C.M.L. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

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nanowire arm segment, (B) purging of gaseous reactants to suspend nanowire elongation, and (C) supersaturation and nucleation of nanowire growth following re-introduction of reactants. As illustrated for the case of silicon, the concentration of silicon-reactant dissolved in the nanocluster catalyst drops during purging and then reaches a maximum upon supersaturation. Steps (A)–(C) can be iterated to link a number of SBUs generating a 2D chain structure.

We first illustrate this approach with the synthesis of 2D silicon nanowire chains. We synthesized ~80 nm diameter silicon nanowires with dominant $\langle 112 \rangle$ axial orientation by gold nanocluster-catalysed vapour-liquid-solid (VLS) method^{17–19} (see Methods and Supplementary Fig. S2). Scanning electron microscope (SEM) images of a typical kinked silicon nanowire structure (Fig. 1c) produced by several iterations of the (A)–(C) cycle designed to yield equal-length segments highlight several notable features. First, well-defined 2D kinked nanowire structures are observed with equal arm lengths, which are consistent with the constant segment growth times, and uniform diameters. Second, the clearly visible gold catalyst at the nanowire tip (Figs. 1c,d) and uniform diameter indicate that growth proceeds via the nanocluster-catalyzed VLS process^{17–19} throughout the whole synthesis. Third, the joint angle is a constant 120° and all SBUs are confined in a single 2D plane consistent with our model (Fig. 1a). Last, the yield of such a kinked 2D chain structure is higher than 40 % for these 80 nm diameter nanowires with purge-times (step-B) of 15 seconds (Supplementary Fig. S3), while the remaining nanowires have a 1D morphology. The kinked nanowire structures could be purified to further enhance yields, and we note that the simple dispersion and deposition process used to prepare samples for analysis leads to a preferential enhancement of the yield on substrates.

To address the potential of *ab-initio* design and synthesis we have prepared kinked silicon nanowires in which the arm length is intentionally varied. A representative SEM image of a structure with 6-distinct segment lengths (Fig. 1d) reveals that the formation of well-defined SBU kinks is independent of the constituent segment lengths within a range of at least 180–2500 nm investigated. Analysis of the segment lengths in uniformly kinked nanowire samples yields a linear dependence of segment length on the axial growth time (Fig. 1e), further supporting our well controlled VLS growth. The slope of the linear fit yields a nanowire axial growth rate of 870 nm/min under current steady state conditions (Fig. 1e, inset and Methods). The differential segment length data extracted from Figure 1d is also plotted (magenta squares) and agrees very well with the data acquired from the kinked nanowires with uniform segments, demonstrating a high level of control for independent syntheses and, correspondingly, the capability for *ab-initio* design and synthesis. We also note that these results, which show that segment length is fully determined by growth time, are distinct from self-organized growth models used to explain oscillatory saw-tooth faceting in nonpolar silicon nanowires⁹ or twinning superlattices in $\langle 111 \rangle$ B-oriented III–V nanowires^{6–8}.

We have also elucidated the atomic level structure of the 2D kinked nanowires using transmission electron microscopy (TEM). A representative TEM image (Fig. 2a) of a multiply-kinked silicon nanowire and selected area electron diffraction (SAED) patterns recorded from nonadjacent joints (Fig. 2b) show that the entire nanostructure is single

crystalline and that the arms and joints are free of bulk dislocations and defects. The SAED patterns from kink positions **I** and **II**, which are separated by ca. 3 μm and 2 intervening kinks, can be indexed for $\langle 111 \rangle$ zone axis and show that (i) the 2D chain structure extends in the $\{111\}$ plane, (ii) confirm that the segments grow along the $\langle 112 \rangle$ direction in a coherent manner. These observations are consistent with our orientation controlled nanowire growth and SBU model (Fig 1a).

TEM images of a single kink (Figs. 2c and 2d) further illuminate key SBU features. First, images demonstrate that there are no atomic-scale twin defects or stacking faults, confirming a single crystal structure across the complete arm-joint-arm junction. This is distinct from other recent reports of modulated nanowires such as twinning superlattices^{6–8} that comprised of twin planes and/or stacking faults. Furthermore, the SBU reported in our work is unique in that it preserves crystallographic orientation and composition in arms over multiple kinks, in contrast to single kinks observed previously^{20, 21}, where the arms had either different growth directions²⁰ or compositions²¹. Second, the joint has a quasi-triangular structure with $\{111\}$ top/bottom facets and two $\{112\}$ side facets joining the adjacent arms. Last, the nanowire growth direction changes during growth of the kink, following $\langle 112 \rangle_{\text{arm}}$ to $\langle 110 \rangle_{\text{joint}}$ to $\langle 112 \rangle_{\text{arm}}$.

To shed light on the mechanism and limits of the single crystalline kinked junction formation, we characterized the kink frequency as a function of key parameters, including nanowire diameter and purge time. The kink frequency is defined as $P_{\text{kink}} = N_k/N_t = N_k/(N_k + N_s)$, where N_t , N_k and N_s denote the number of total designed junctions, observed kink junctions, and observed straight and node-like junctions, respectively. Under optimal growth conditions (Methods), both 80 and 150 nm silicon nanowires (Fig. 3a) show a high probability of kinks with a regular zigzag geometry. When the purge time of step-B (Fig. 1b) is reduced from optimal to 3 or 1 s, nodes or incipient kinks (Fig. 3b) are observed at the positions expected for kinks based on elongation time and growth rate. Higher resolution SEM or TEM define the nodes as slightly larger diameter regions with lengths of ~ 50 nm. A summary of results for 80 and 150 nm diameters obtained for 1, 3 and 15 s purges (Fig. 3c) quantifies these observations and shows that this reduced kink frequency with decreasing purge times is more pronounced in larger diameter nanowire samples. These results are consistent with reactant concentration drop from the nanocluster catalyst being critical for kink formation since the relative concentration drop will be smaller at fixed purge time in larger versus smaller diameter nanowires²².

Overall, the above studies suggest kink formation can be qualitatively explained by the proposed step-wise model shown in Figure 3d. In step-1, the reactant concentration drops in the supersaturated catalyst during the purge, and if the concentration is reduced sufficiently, elongation will cease. When reactant is re-introduced in step-2, the catalyst can become supersaturated again and undergo heterogeneous nucleation^{23,24} and growth. For short purge times and larger diameter nanowires, the reactant concentration is sufficient for elongation to continue; however, as shown in *in-situ* TEM studies²² this situation can lead to a flattening of the catalyst nanodroplet and increase in nanowire diameter consistent with formation of nodes (Fig. 3b, marked with blue stars). In step-3, growth proceeds with preservation of the most stable $\{111\}$ facets²⁵ thus implying that the heterogeneous

nucleation should occur preferentially at the active $\{110\}$ edges²⁶ of the three phase boundary²⁴. This model yields a transition from the $\langle 112 \rangle$ to $\langle 110 \rangle$ direction about the $\langle 111 \rangle$ axis. This growth along $\langle 110 \rangle$ is transient since this direction is not thermodynamically favourable in this diameter regime^{19,20} (Supplementary Fig. S2), and in step-4, the kink is completed with a transition to another $\langle 112 \rangle$ direction thus completing a single SBU with coherent arm growth directions. We did not observe $\langle 112 \rangle$ to $\langle 111 \rangle$ growth switching²⁰ in our kinked structures, most likely because the growth of a $\langle 111 \rangle$ segment requires the formation of six new $\{112\}$ facets⁹ and the disappearance of two stable $\{111\}$ facets²⁶ of the initial $\langle 112 \rangle$ segment.

While additional experiments will be necessary to clarify details of the kink formation hypothesis in our proposed growth model, we note that this model now enables the design and synthesis of specific structures in silicon nanowires and, more generally, nanowire systems with distinct compositions. To illustrate this point, we first designed and synthesized $(\text{kink-node})_m$ and $(\text{kink-node})_m(\text{kink})_n$ modulated silicon nanowire structures, where m and n are indices denoting the number of times the structural unit's growth is repeated. We chose 150 nm gold as catalysts, 15 and 1 s as purge durations (Fig. 3c) for the growth of kinks and nodes, respectively. Notably, SEM images of the $(\text{kink-node})_m$ structure (Fig. 3e, **I** and **II**) show that the nodes (highlighted with yellow stars) are reproducibly inserted between kinks over multiple modulations. These results also show that the formation of individual kinks or nodes is independent of adjacent elements and is controlled by growth conditions. This latter point and possible control is further demonstrated by the synthesis of coherent $(\text{kink})_8$ SBUs following modulated $(\text{kink-node})_4$ units (Fig. 3e, **III**). Interestingly, the observation of coherent zigzag chain structures suggests that 'steering' of kinks is not random and might be due, for example, to a minimization of stress or maintenance of the centre-of-mass of the whole structure. Although additional studies will be required to understand the coherence in multiply-kinked structures, we believe that these results already highlight an emerging potential of our 'nanotectonic' approach to generate in a predictable manner complex 2D nanowire structures.

In addition, we have used our model for the designed synthesis of 2D kinked nanowire structures in other materials. For example, SEM images (Fig. 4a) of Ge nanowires grown using the iterative approach of Figure 1a (see Methods) show nanowires with well-defined kinks, where the kink angle, 120° , is consistent with that for the SBU. TEM images (Fig. 4b) further demonstrate that (i) the growth direction of the arms of the 2D kinked Ge nanowires are along the $\langle 112 \rangle$ direction and (ii) the joint is single crystalline. These structural details are consistent with the general features observed in kinked silicon nanowires (Fig. 1 and Fig. 2). Our model also predicts that the arm-joint-arm kink SBU could be realized in very different materials such as the wurtzite phase of the group II–VI semiconductor CdS. Notably, designed iterative modulation of the growth of $\langle 11\bar{2}0 \rangle$ direction CdS nanowires yields a regular 2D kinked structure with 120° kink angle as shown in Figure 4c. TEM images (Fig. 4d) demonstrate that the CdS 2D kinked nanowire structure is single-crystalline with arms all along the $\langle 11\bar{2}0 \rangle$ direction of the wurtzite phase. Finally, we suggest our approach could also be used for the designed synthesis of 2D kinked group III–V nanowire

materials such as GaN nanowires, which have been reported with almost pure $\langle 11\text{--}20 \rangle$ orientation⁴.

These results highlight an emerging potential of our bottom-up ‘nanotectonic’ approach to generate more complex nanowires with potentially unique function ‘integrated’ at the nanoscale in the topologically-defined points of the kinks. We illustrate this capability by combining our iterative growth approach with additional modulation of dopant to vary electronic characteristics in a well-defined manner with respect to the kinks. A kinked Si nanowire SBU with integrated *n*- and *p*-type arms was synthesized by switching phosphine and diborane dopants during the kink growth sequence (Methods). Current-voltage (*I*–*V*) data recorded on a representative single kink device (Fig. 5a) reveal a clear current rectification in reverse bias with an onset at forward bias voltage of ~ 0.6 V, consistent with the synthesis of a well defined *p*–*n* diode within the kinked structure. Moreover, an electrostatic force microscopy image of a typical kinked *p*–*n* nanowire in reverse bias (Fig. 5b) showed that the voltage drop occurs primarily at the designed *p*–*n* junction localized and labelled by the kink during growth.

In addition, our concept can be extended to design and synthesis of nanowires with distinct functionality at sequential kinks. A representative atomic force microscopy image of a double kink structure synthesized with n^+ and *n* dopant profiles at the two kink joints (Fig. 5c) shows that the characteristic SBU described above is unaffected by multiple modulations of dopant concentration. Notably, scanned gate microscopy data (Fig. 5d) demonstrates enhanced (decreased) nanowire conductance as the tip with positive (negative) gate potential is scanned across the designed *n*-type segment immediately adjacent to the upper-left kink junction, thus confirming the integration of an *n*-type field-effect transistor at a well-defined and recognizable point on the structure. The absence of gate response from the lower-right kink junction (Fig. 5d) further shows that the single crystalline kink structure itself will not alter the electrical transport properties. We believe that these synthetic results and demonstrated topologically-defined functional devices represent a significant advance towards the realization of *ab-initio* designed and ‘self-labelled’ 2D nanowire structures. Such designed and self-labelled 2D nanowire structures may open up unique applications in bottom-up integration of active devices in nanoelectronics, photodetector arrays, multiplexed biological sensors, and the presentation of multi-terminal nanodevices in 3D.

Methods

Nanowire synthesis

Single-crystalline kinked nanowires were synthesized by the nanocluster-catalyzed VLS method described previously^{18,19} in quartz tube connected to gas manifold and vacuum pump and heated by a temperature controlled tube furnace. Monodisperse gold nanoparticles (Ted Pella) were dispersed on SiO₂/Si or sapphire growth substrates (Au surface coverage: 0.01–0.1 particles/ μm^2), which were placed within the central region of the quartz tube reactor. Nanowires grown on both substrates yielded similar kink morphologies and yields. The silicon (Si) nanowires were synthesized at 450–460 °C using silane (SiH₄) as the silicon reactant source, hydrogen (H₂) as the carrier gas, and phosphine (PH₃, 1,000 p.p.m. in H₂) and diborane (B₂H₆, 100 p.p.m. in H₂) as the *n*- and *p*-type dopants. In a typical synthesis of

uniform *n*-type, 80 nm kinked silicon nanowires, the flow rates of SiH₄, PH₃ and H₂ were 1–2, 210 and 60 standard cubic centimetres per minute, respectively, and the total pressure was 40 torr and purge duration was 15 s; the minimum pressure during the purge cycle was ca. 3×10^{-3} torr. The dopant feed-in ratios (silicon:boron/phosphorus) in kinked *p*-*n* silicon nanowires were 500:1 for both *p*- and *n*-type segments. In *n*⁺-kink-*n*⁺-kink-(*n*-*n*⁺) dopant modulated silicon nanowires, the silicon-phosphorus feed-in ratios were 200:1 and 10000:1 for *n*⁺- and *n*-type segments, respectively, and the *n*- segment was grown for 30 s. Germanium nanowires were synthesized at 270–290 °C, 40 torr, with germane (GeH₄, 10 % in H₂) and H₂ as the reactant and carrier gas, respectively. Cadmium sulphide nanowires were grown in a three-zone furnace by evaporating CdS power at 650–720 °C, with nanowire growth by gold nanocluster catalyzed VLS method at 550–500 °C. The purge cycle used to form kinks in the germanium and cadmium sulphide nanowires was typically 15 s.

Structure characterization

Zeiss Ultra55/Supra55VP field-emission SEMs and JEOL 2010 field emission TEM were used to carry out SEM and TEM analyses, respectively. For sample preparation, kinked nanowires were gently sonicated in isopropyl alcohol and dispersed onto heavily doped silicon substrates (100 nm oxide/200 nm nitride, 1–10 Ω·cm resistivity, Nova Electronic Materials, Carrollton, TX) or lacey carbon grids (Ted Pella).

Device fabrication and measurement

Devices were fabricated on silicon substrates (Nova Electronic Materials, *n*-type 0.005 Ω·cm) with 100 nm thermal oxide and 200 nm silicon nitride at the surface. Devices were defined by electron-beam lithography followed by Ti/Pd (1.5 nm/100 nm) contact deposition in a thermal evaporator. Current-voltage (*I*-*V*) data were recorded using an Agilent semiconductor parameter analyzer (Model 4156C) with contacts to devices made using a probe station (Desert Cryogenics, Model TTP4). Electrostatic force microscopy and scanned gate microscopy measurements were carried out with a Digital Instruments Nanoscope IIIa MultiMode AFM and metal coated tips (Nanosensors, PPP-NCHPt). The electrostatic force microscopy surface potential maps and scanned gate microscopy conductance maps were acquired in lift mode with lift heights of 40 and 20 nm, respectively. In the surface potential measurements, the *p*-*n* diode was reverse-biased at 5 V and the tip voltage was modulated by 3V at the resonance frequency. In scanned gate measurements, the tip functions as a local gate $V_{tip} = \pm 10$ V, and the conductance versus position provides a measure of local accumulation or depletion of carriers in the device.

Supplementary Material

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Figure 1. Design and controlled synthesis of multiply-kinked nanowires

a, Schematic of a coherently kinked nanowire and the secondary building unit (SBU) which contains two arms (blue) and one joint (green). The multiply-kinked nanowires (middle panel) are derived from the corresponding 1D nanowire by introducing the joints at the points indicated by dashed lines (upper panel). The subscript *c* and *h* denote *cubic* and *hexagonal* structures, respectively. **b**, Cycle for the introduction of a SBU by step-wise synthesis. The colour gradient accompanying the innermost blue arrows indicates the change of silicon concentration in nanocluster catalyst during synthesis of a kinked silicon nanowire. **c**, SEM image of a multiply-kinked 2D silicon nanowire with equal arm segment lengths; scale bar is $1 \mu\text{m}$. The yellow arrow highlights the position of the nanocluster catalyst. **d**, SEM image of a multiply-kinked silicon nanowire with decreasing arm segment lengths; scale bar is $1 \mu\text{m}$. The growth durations are 30, 60, 90, 120, 150 and 180 s for segments 1 to 6, respectively. The yellow arrow highlights the position of the nanocluster catalyst. SEM images shown in **c** and **d** were acquired without substrate tilting, and the electron beam perpendicular to the 2D plane of the multiply-kinked nanowires. **e**, Plot of segment length vs. growth time. Each blue diamond represents average segment length data (error bars: ± 1 standard deviation) from a sample containing nanowires with uniform segment lengths between kinks. Green line is a linear fit to these data. Magenta solid squares are data points taken from the nanowire shown in **d**. Inset, growth pressure variation during kink synthesis. Black solid sphere and square denote the start of purging and re-introduction of reactants, respectively.

Figure 2. Crystallographic structure of kinked silicon nanowires

a, Bright-field TEM image of a multiply-kinked silicon nanowire; scale bar corresponds to 1 μm . The green (region-I) and red (region-II) dashed circles highlight nonadjacent kinks where diffraction data was recorded. The yellow arrow highlights the position of the nanocluster catalyst. **b**, Selected area electron diffraction (SAED) patterns recorded from regions **I** and **II** in **a**. The SAED patterns were recorded along the $\langle 111 \rangle$ zone axis. **c**, TEM image of a single kink with crystallographic directions and facets indicated by arrows and dashed lines, respectively; the scale bar is 50 nm. The green (region-I) and blue (region-II) open squares highlight regions of the joint and one arm where high resolution images were recorded. **d**, Lattice-resolved TEM images from regions **I** and **II** in **c**; the scale bars are 5 nm. Dashed lines and arrows denote crystallographic planes and growth directions, respectively. All TEM images and SAED patterns were acquired with the electron beam perpendicular to the 2D plane of the kinked nanowires.

Figure 3. Mechanistic studies of kinked nanowire growth

a, SEM images of 150 (upper) and 80 nm (lower) diameter kinked silicon nanowires grown with periodic 15 s purges; scale bar is 1 μ m. **b**, TEM images at low (left panel) and high (right panel) magnification of one 80 nm diameter silicon nanowire segment subjected to a 1 s purge. The blue stars mark incipient kinks or nodes, and dashed square corresponds to the region where right panel was recorded. Scale bars are 500 and 50 nm. **c**, Kink frequency (P_{kink}) histogram for 80 and 150 nm diameter silicon nanowires grown with different purge durations. Green, red and blue bars denote results from 1, 3 and 15 s purges, respectively, and are averaged over at least 15 multiply-kinked nanowires. **d**, Schematic illustrating the key stages of kink formation. Arrows 1–4 denote purge, reintroduction of reactant, joint growth and subsequent arm growth, respectively. **e**, SEM images of 2D silicon nanowires with modulated kinks and incipient kinks (starred nodes). **I** corresponds to a designed (kink-node) $_m$ structure, **II** is zoom of one node from the region indicated by the dashed yellow square in **I**, and **III** corresponds to a (kink-node) $_m$ (kink) $_n$ structure, where m and n are integers. The angle between the norm of kinked nanowire plane and the electron beam in **III** is $\sim 50^\circ$. All other images were acquired with the electron beam perpendicular to the 2D plane of the kinked nanowires. The scale bars in **I**, **II** and **III** are 1, 0.2 and 1 μ m, respectively.

Figure 4. Generality of kinked nanowire synthesis

a, SEM image of one multiply kinked germanium nanowire; scale bar is 1 μm . **b**, Lattice-resolved TEM of the joint region of a representative germanium nanowire kink; scale bar is 5 nm. Inset highlights one SBU with arrows corresponding to $\langle 112 \rangle$ growth directions and red square to region where high-resolution image was recorded. Inset scale bar is 50 nm. **c**, SEM image of one multiply kinked cadmium sulphide nanowire; scale bar is 1 μm . **d**, Lattice-resolved TEM of the arm region of a representative cadmium sulphide adjacent to the kink joint; scale bar is 5 nm. Inset highlights two SBU with arrows corresponding to $\langle 11\bar{2}0 \rangle$ growth directions and red square to region where high-resolution image was recorded. Inset scale bar is 50 nm. All images were acquired with the electron beam perpendicular to the 2D plane of the kinked nanowires.

Figure 5. Topologically-defined nanoelectronic devices

a, I–V data recorded from a kinked p - n silicon nanowire device. Inset, SEM image of the device structure; scale bar is 2 μm . **b**, Electrostatic force microscopy image of a p - n diode reverse-biased at 5 V. The AFM tip voltage was modulated by 3 V at the cantilever-tip resonance frequency. The signal brightness is proportional to the nanowire device surface potential, and shows an abrupt drop around the kink position. The dashed lines mark the nanowire position. Scale bar is 2 μm . **c** and **d**, AFM and scanning gate microscopy images of one n^+ -kink- n^+ -kink- $(n-n^+)$ dopant modulated double-kinked silicon nanowire structure. The scale bar in **c** is 2 μm . The scanning gate images were recorded with a V_{tip} of 10 V (**I**) and –10 V (**II**), respectively, and V_{sd} of 1 V. The dark and bright regions correspond to reduced and enhanced conductance, respectively. The black dashed lines mark the nanowire position.