Direct oriented growth of armchair graphene nanoribbons on germanium

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Graphene can be transformed from a semimetal into a semiconductor if it is confined into nanoribbons narrower than 10 nm with controlled crystallographic orientation and well-defined armchair edges. However, the scalable synthesis of nanoribbons with this precision directly on insulating or semiconducting substrates has not been possible. Here we demonstrate the synthesis of graphene nanoribbons on Ge(001) via chemical vapour deposition. The nanoribbons are self-aligning from the Ge$(110)$ directions, are self-defining with predominantly smooth armchair edges, and have tunable width to $<10$ nm and aspect ratio to $>70$. In order to realize highly anisotropic ribbons, it is critical to operate in a regime in which the growth rate in the width direction is especially slow, $<5$ nm h$^{-1}$. This directional and anisotropic growth enables nanoribbon fabrication directly on conventional semiconductor wafer platforms and, therefore, promises to allow the integration of nanoribbons into future hybrid integrated circuits.

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Graphene nanoribbons are excellent charge conductors that can exhibit high current-carrying capacity and novel magnetic and spin-polarized edge states depending on their crystallographic orientation, edge structure and width. Unlike continuous two-dimensional graphene, which is semimetallic, one-dimensional (1D) graphene nanoribbons can be semiconducting, allowing for substantial modulation of their conductance and enabling their application in semiconductor logic, high-frequency communication devices, optoelectronics, photonics and sensors in which a bandgap is needed to achieve high performance. Their bandgap roughly varies inversely with ribbon width and the largest bandgaps are expected for ribbons with armchair edge orientation.

While achieving a ribbon width of <10 nm is necessary to induce a technologically relevant bandgap that is substantially greater than $k_B T$ of 25 meV at room temperature, sub-10 nm resolution is beyond the limits of conventional optical and electron-beam lithography. Moreover, top-down lithographic techniques in which ribbons are etched from continuous graphene sheets result in nanostructures with relatively rough, defective edges, which lead to Coulomb blockade and localized electronic and phonon states and, consequently, degrade the high charge carrier mobility and thermal conductivity of graphene.

These deficiencies, in part, can be overcome, via bottom-up organic synthesis on metal surfaces and in solution as well as by unzipping graphite and carbon nanotubes in solution, to yield ribbons with sub-10 nm width and smooth edges. However, surface-assisted organic synthesis yields short ribbons (~20 nm) and unzipping graphite and carbon nanotubes does not offer control over the ribbon crystallographic orientation. Moreover, the controlled placement and alignment of ribbons onto substrates from solution has proven to be difficult.

Scalable nanoribbon fabrication has also been reported via epitaxial growth on templated SiC nanofacets and by chemical vapour deposition (CVD) on surface features, such as steps, twins and trenches, as well as on patterned catalysts in which growth is confined to predetermined areas that define the ribbon dimensions. However, with these approaches, ribbons with sub-10 nm width have not been demonstrated and the catalyst template determines the ribbon edge structure rather than a more precise self-defining growth mechanism.

Here we show that the CVD of graphene on Ge(001) can be controlled to yield oriented nanoribbons with sub-10 nm width and smooth armchair edges. Previous work on integrating graphene with Ge has primarily focused on large-area graphene monolayers. For example, continuous graphene films have been transferred onto Ge from other substrates. Furthermore, continuous graphene monolayers have been grown via CVD directly on Ge(001) by Wang et al. and Ge(110) and Ge(111) by Lee et al. However, in these previous studies, nanoribbons were not observed in partial growth experiments. In this work, we report that high aspect ratio nanoribbons can be directly grown on the Ge(001) facet by tailoring the CVD conditions to maximize the anisotropy of crystal growth. It is critical to operate in a regime in which the growth rate is especially slow, $<5 \text{ nm h}^{-1}$ in the width direction. Nanoribbons are grown at atmospheric pressure using various growth temperatures (860 $< T < 935 \text{ C}$), CH$_4$ mole fractions (3.7 $< x_{\text{CH}_4} < 1.6 \times 10^{-3}$), and H$_2$ mole fractions (0.17 $< x_{\text{H}_2} < 0.33$), as summarized in Supplementary Table 1. By tuning $T$, $x_{\text{CH}_4}$, $x_{\text{H}_2}$ and the growth time ($t$), the growth anisotropy is tailored to yield ribbons from the bottom-up with controlled width ($w$), length ($l$) and aspect ratio. Using conditions in which the anisotropy is maximized, isolated ribbons are prevalent on the Ge(001) surface even after $t > 18$ h. In contrast, Wang et al. used a relatively fast growth rate in which continuous graphene films were synthesized on Ge(001) in $t < 100$ min.

**Results**

**Growth behaviour.** Several general observations are made regarding graphene growth on Ge(001) by analysing representative scanning electron microscopy (SEM), atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) images in Fig. 1a–c. Following nucleation, graphene crystals evolve anisotropically, resulting in nanoribbons with high aspect ratio

![Figure 1](image-url)
and smooth, straight edges. Raman spectroscopy indicates that the 2D:G ratio and the 2D peak full-width-at-half-maximum are 6.0 and 28 cm⁻¹, respectively, confirming that the nanoribbons are monolayer graphene (Supplementary Fig. 1). The ribbons preferentially orient closely along the (110) directions of the Ge(001) template, resulting in two ribbon orientations that are approximately perpendicularly aligned. These two orientations exist with equal probability. For ribbons with w < 10 nm, the short ribbon edges form 60, 90 or 120° angles with the long ribbon edges. However, for wider ribbons, only angles of 60 and 120° are observed, indicating that all edges are oriented along equivalent crystallographic directions of graphene. While as high as 90% of the graphene crystals that nucleate evolve as ribbons, more compact graphene crystals with lower aspect ratio and edges that are not aligned along Ge(110) directions are also observed. Interestingly, the Ge underneath the ribbons is nano facetted, which is studied further below.

Growth kinetics and evolution. We quantify the growth kinetics to gain insight into the processes that determine the ribbon size and aspect ratio using constant T of 910°C, xCH₄ of 0.0092 and xH₂ of 0.33. Both w and l increase with t, along with the ribbon-to-ribbon variation in w and l, which is quantified by the range of the box and whiskers in Fig. 1d,e. The mean growth rates in the w and l directions, R_w and R_l, respectively, are compared in the insets of Fig. 1d,e (where w and l increase on average at twice R_w and R_l). Initially, R_l is 90 nm h⁻¹ whereas R_w is only 5 nm h⁻¹, giving rise to the anisotropic ribbon evolution. While R_l is relatively constant with time, R_w increases to > 10 nm h⁻¹ after several hours. Accordingly, the mean aspect ratio decreases from 20 to 10 with increasing t (Fig. 1f). Stopping growth after t of 1 h results in ribbons with average w of 9.8 nm (Fig. 1g), which is below the resolution of optical and typical electron-beam microscopy (LEEM) and diffraction (LEED), and we anticipate that even narrower w are obtained at earlier t. Figure 1c shows an example of a nanoribbon with w of 7 nm and l of 160 nm.

The effects of xCH₄, xH₂ and T on the nanoribbon growth rate and the resulting anisotropy are also quantified. The growth rates increase as xCH₄ increases (Fig. 2a), xH₂ decreases (Fig. 2b), and T increases (Supplementary Fig. 2). Each of these parameters can be independently tuned to vary R_l over an order of magnitude from 30 to 300 nm h⁻¹. The anisotropy varies inversely with R_l independent of whether xCH₄ or xH₂ is changed (Fig. 2c). Thus, a critical parameter for realizing high aspect ratio nanoribbons is to operate in a regime in which growth is slow. For example, at low xCH₄ of 0.0066 and high xH₂ of 0.33, not only is a slow R_l of 40 nm h⁻¹ achieved, but also a much slower R_w of 1.4 nm h⁻¹, yielding ribbons with an aspect ratio of 30, on average, and as high as 70 (Supplementary Fig. 3). Minimizing R_w also makes it possible to tailor w with high precision. Empirical rate laws are identified (insets of Fig. 2a,b), indicating that R_l scales as xCH₄ and xH₂ (ref. 34). Furthermore, an Arrhenius temperature dependence is observed with an activation energy of 7.2 ± 0.4 eV (Supplementary Fig. 2). For comparison, the activation energy for graphene growth on Cu is only 1–3 eV (ref. 35). However, graphene growth on Cu at atmospheric pressure yields hexagonal crystals instead of nanoribbons (ref. 36), highlighting that different mechanisms control growth.

We also find that the 1D nature of growth is insensitive to the bulk Ge dopant concentration (N₁₀< 1.5 × 10¹⁸ cm⁻³), Ge surface treatment prior to synthesis (OH, H and Cl functionalization), and annealing time before growth (Supplementary Figs 4–6). Nanoribbons are not observed on Ge(110) nor Ge(111) under any growth condition (Supplementary Fig. 7).

Low-energy electron microscopy and diffraction. Low-energy electron microscopy (LEEM) and diffraction (LEED) are used to determine the orientation of the graphene lattice with respect to the underlying Ge and with respect to the ribbon edges. The overlaid LEED patterns in Fig. 3a taken at 121 and 135 eV establish the Ge[110] and [110] directions. The LEED pattern in Fig. 3b obtained at 67 eV shows that the graphene lattice primarily exists within two families of crystallographic orientations, denoted by the orange and purple hexagons. Dark-field imaging in Fig. 3c indicates that the purple family of diffraction spots originates from ribbons that are oriented with their long axis approximately parallel to Ge[110] whereas the orange family of spots originates from ribbons that are oriented with their long axis approximately parallel to Ge[110]. Both of these families of ribbons have edges that are macroscopically aligned with the armchair direction of graphene. This armchair edge orientation is unique because graphene crystals grown on Cu and Ni typically have edges that are aligned along the zigzag direction of graphene (ref. 35, 37).

Within each family, there are two unique graphene orientations that are rotated 2.9 ± 0.4° (~3°) relative to the Ge[110] directions, as indicated by the diffraction spots belonging to the orange family that are circled in red and blue in Fig. 3b. These nanoribbon orientations are depicted in Fig. 3d. Dark-field imaging in Fig. 3c indicates that some of the ribbons are single crystalline, corresponding to either the +3° or −3° graphene orientation, whereas others are bi-crystalline, in which the crystal lattice of one half of the ribbon is rotated by 2 × 3° = 6° with respect to the other half. This indicates that the nanoribbons nucleate in their centre and then grow in opposite directions.

Figure 2 | Effect of precursor composition on graphene nanoribbon growth on Ge(001). (a,b) R_l versus xCH₄ (a) and xH₂ (b). Insets of a,b contain the same data plotted on a log–log scale with best fit line (red), which is used to find the empirical rate laws. (c) Aspect ratio of ribbons with w of 30 ± 5 nm plotted against R_l for conditions in which xCH₄ (blue triangles) and xH₂ (red circles) are varied. The ribbons in a,c are grown at 910°C with xH₂ of 0.33 and xCH₄ varied from 0.0066 to 0.016. The ribbons in b,c are grown at 910°C with xCH₄ of 0.0066 and xH₂ varied between 0.22 and 0.33. Error bars indicate standard deviation.
along their length. These dynamics potentially explain why the ribbons are elevated in their centre (Fig. 1c); the sublimation of Ge may be locally suppressed under the ribbons as they grow. Interestingly, the lattice of the non-ribbon graphene crystals with lower aspect ratio and edges not aligned on Ge[110], like the one observed in Fig. 1a, is rotated with respect to the lattice of the nanoribbons, typically by 15° as observed in Fig. 3b. This difference indicates that the anisotropic nanoribbon growth is driven only when there is a specific relative orientation between the graphene lattice and the Ge(001) surface.

Scanning tunneling microscopy. Ultra-high vacuum STM is performed to substantiate the LEED data and to determine the atomic nature of the graphene nanoribbon edges on Ge(001). The STM image and its corresponding fast Fourier transform (FFT) in Fig. 4a indicate that the ribbon edges are straight and parallel to the armchair direction of graphene with little edge roughness and that the graphene lattice is rotated 3° from the Ge(110) directions, consistent with the LEED data. The Ge underneath the nanoribbons retains the common (2 × 1) dimer reconstruction (Fig. 4b–d) even after ambient exposure. Contamination of the bare Ge surface upon exposure to ambient often precludes precise topographical imaging of the nanoribbon edge structure. Using the topographic data alone, we can set an upper limit on the edge roughness. For example, the representative 40 nm ribbon segment in Fig. 4a has roughness of <0.5 nm (two lattice constants of graphene). However, we can learn more about the edge structure from quantum interference patterns caused by intervalley backscattering (Fig. 4e) of charge carriers at the ribbon edges. The ring-like shapes with a (√3 × √3)R30° unit cell highlighted with the rhombuses in Fig. 4g and the armchair-like patterns with periodicity (K_a) of 3.7 Å in Fig. 4g are consistent with electron backscattering at armchair edges16,38 and are clearly revealed by the prominence of the K/K' points in the FFT in Fig. 4f. The presence of these coherent interference patterns combined with the small line edge roughness indicates that the edges consist primarily of smooth armchair segments. The interference patterns stay into the interior of the ribbons with length scales comparable to graphene on SiC38 and metals39. The atomic structure of the hexagonal graphene lattice is observed past these decay lengths in the interior of the nanoribbons (Fig. 4g).

Charge transport measurements. Charge transport measurements are conducted to investigate the electrical properties of 33 nanoribbons using a field-effect transistor geometry (Fig. 5). The ribbons are relatively wide (w = 10 nm), because these ribbons are more conducive to transfer onto insulating SiO_2/Si wafers (Fig. 5e). Transfer is required to measure the electrical properties of the ribbons independent of parallel conduction pathways through the Ge substrates used for growth.

The magnitude of the ribbon conductance modulation caused by varying an applied back-gate voltage (that is, the on/off ratio) generally increases as w is reduced below 15 nm (Fig. 5a,d), consistent with the opening of a bandgap that scales inversely with w. The on/off ratios are comparable to those of high-quality chemically exfoliated nanoribbons of similar w (for example, on/off of ~1, ~5 and ~100 have been demonstrated for w of ~50, ~20 and ~10 nm, respectively)20. However, the largest gains in on/off ratio are not expected until w is reduced to 3–5 nm.

The on-state conductance (Fig. 5b) and transconductance (Fig. 5c), normalized by w, are not correlated with w and, thus, do not generally deteriorate as w is decreased. The nanoribbon channel resistance and the Pd–nanoribbon contact resistance are not separately quantified. However, the on-state conductance is high (generally ranging from 500 to 5,000 μS μm⁻¹) and the on-state resistance (average of ~700 Ω μm) is similar to literature values for Pd–graphene contact resistance (150–1,640 Ω μm)42–49. Therefore, the data suggest that at the relatively short channel length used here of <220 nm, charge transport is not limited by edge scattering or by channel resistance, but instead by the Pd–nanoribbon contacts. The variability in the on-state conductance (Fig. 5b) and the transconductance (Fig. 5c) data
is likely caused by contact-length variability, which increases as the ribbons become narrower and thus shorter (Supplementary Discussion).

Characterization of the graphene/germanium interface. As growth progresses, the ribbons eventually merge to form a continuous graphene film that is self-limiting to a monolayer. We analyse these continuous films to characterize the graphene/Ge interface and the Ge nanofaceting beneath graphene. The films have negligible Raman D-band intensity (Supplementary Fig. 10), indicating an sp² graphene lattice with low defect density and a high degree of planarity. These continuous films can be peeled off of the Ge(001) surface using a thin Au layer, indicating that the Ge-Ge interaction strength is only when the armchair direction of graphene is rotated 3° from the [110] direction.

Germanium nanofacet formation. As previously observed in Figs 1b,c and 4a, the Ge surface selectively forms nanofacets underneath the nanoribbons. These hill-and-valley structures are more stable in ambient conditions, even at 200 °C for 24 h.

Discussion

Our experimental data, which show that growth is anisotropic only when the armchair direction of graphene is rotated 3° from the [110] direction, provide insight into the mechanisms..
governing the 1D nature of growth. It is likely that this crystallographic relationship is set during the early stages of nucleation; as the graphene nucleus becomes larger, the energy barrier associated with its rotation significantly increases, which, consequently, fixes the orientation of the nanoribbon lattice during the subsequent growth52. The Ge(001) surface consists of two types of terraces that have the same structure but are rotated 90° with respect to each other. It is plausible that on one set of terraces, the armchair direction of the graphene nuclei is rotated 3° from Ge[110] and on the other set of terraces, the armchair direction is rotated 3° from Ge[110], giving rise to the two families of orientations observed in the LEED and STM data.

After nucleation, several factors could drive anisotropic ribbon evolution. While step edges may play a role in setting the crystallographic orientation of the nuclei on each terrace, subsequent preferential growth along step edges cannot solely account for the formation of ribbons with smooth edges over long segments. Furthermore, we do not observe residual nanoparticles at the ribbon ends or tapered ribbon growth that might indicate that the ribbon evolution is driven by a catalyst particle like in conventional nanowire growth 53. Anisotropic diffusion of intermediate hydrocarbons on the Ge surface cannot alone account for the ribbon evolution because low aspect ratio crystals are also observed.

We hypothesize that the anisotropic growth is due to preferential attachment of intermediate hydrocarbons from the Ge surface to the short (faster growing) ribbon edges over the long (slower growing) ribbon edges, which is consistent with the observation that the low aspect ratio crystals have different lattice orientation than that of the nanoribbons. During attachment, the transition state and the corresponding energy

![Figure 5](image)

**Figure 5 | Charge transport of graphene nanoribbon field-effect transistors.** (a–c) On/off current ratio (a), on-state conductance per width (Gon/w) (b) and transconductance per width (gm/w) (c) plotted against w. (d) Conductance per width (G/w) plotted against applied back-gate voltage for representative ribbons with w of 52 nm (red), 23 nm (blue) and 12 nm (green), respectively. The transfer curves in d correspond to the data points circled with the same colour in a–c. (e) Scanning electron micrographs of the nanoribbon channels corresponding to the data points in a–c and transfer curves in d with the same colour. Scale bars in e are 100 nm. All measurements are conducted at room temperature in ambient conditions using a source voltage of 0.1 V.

![Figure 6](image)

**Figure 6 | Characterization of continuous graphene films grown on Ge(001).** (a,b) SEM image (a) and AFM topographic map (b) of a graphene monolayer on Ge(001). Scale bars, 200 nm (a,b); height scale bar, 11.8 nm (b). Inset of (b) is height (h) plotted against projected surface distance (d) showing the profile of the facets across the dotted line in b. (c) LEED pattern taken at 19 eV showing the {01} spots from the unreconstructed Ge(001) surface (magenta) and the {00} spots from the Ge facets (cyan).
corresponding to when ribbons begin to outgrow the Ge terrace. The definition of nanoribbons with width \( w \) has been difficult, and progress in nanoribbon research and development. Specifically, ribbons with \( w \) nm are self-aligning, and growth offers precise control over the ribbon structure beyond the orientation and smooth armchair edges. This direct, self-defining growth offers precise control over the ribbon structure beyond the fidelity of top-down lithography and yields a relatively pristine nanoribbon/substrate interface. The ribbons are self-aligning, and ribbons with \( w < 10 \) nm can still be hundreds of nanometres in length, opening the door for exploration of dense nanoribbon arrays as logic, photonic and sensing components in integrated circuits. Improved control over the ribbon placement will enhance the viability of these applications. These results are also technologically important because they enable a scalable, high throughput pathway for integrating nanoribbons directly on conventional large-area semiconductor wafer platforms that are compatible with planar processing, like Ge wafers and potentially epitaxial Ge films on Si (ref. 33) or GaAs (ref. 58) wafers.

**Methods**

**Graphene synthesis.** Before growth, Ge(001) (Wafer World, resistivity > 40 \( \Omega \) cm, miscut < 1°), Ge(110) (University Wafer, resistivity 0.1–0.5 \( \Omega \) cm with Ga or Sb dopants) and Ge(111) (Semiconductor Wafer, resistivity > 30 \( \Omega \) cm) substrates are cleaned via sonication in acetone and isopropanol alcohol for 15 min followed by etching in deionized H\(_2\)O (18 M\(_\circ\) cm) at 90 °C for 15 min. The Ge substrates are loaded into a horizontal tube furnace with a quartz tube inner diameter of 34 mm and the system is evacuated to \( 10^{-6} \) Torr. The system is then filled to atmospheric pressure with a mixture of Ar (99.999%) and H\(_2\) (99.999%) using a constant total flow rate of 300 s.c.c.m. The Ge samples are annealed for 30 min at the selected growth temperature and then CH\(_4\) (99.99%) is introduced to begin the synthesis. In order to terminate growth, samples are rapidly cooled in the same atmosphere used during synthesis by sliding the furnace away from the growth region. Specific growth conditions are provided in Supplementary Table 1.

**Graphene transfer.** In order to transfer the ribbons from Ge to SiO\(_2\)/Si for Raman spectroscopy and charge transport measurements, poly(methyl methacrylate) (PMMA) is spin coated onto the graphene/Ge substrate. The PMMA/graphene/Ge stack is floated on a solution of 28:1:1 H\(_2\)O:H\(_2\)O\(_2\):EtOH to etch the Ge layer. The PMMA/graphene/Ge stack is transferred to H\(_2\)O to clean the ribbons and then lifted out of the H\(_2\)O using a SiO\(_2\)/Si substrate. The PMMA is dissolved in acetone and the sample is washed with isopropanol alcohol.

**Characterization.** After growth, the samples are characterized with SEM (Zeiss LEO 1530) and AFM (Veeco MultiMode SPM) in tapping mode. For each nanoribbon synthesis, the \( w \) and \( l \) of ~250 ribbons are measured from SEM images using ImageJ. Raman spectroscopy (Thermo Scientific DXRxi) in Supplementary Fig. 1 is performed using excitation wavelength of 532 nm, power of 10 \( mW \) and spot size of 0.6 \( \mu m \). Graphene degradation studies in Supplementary Fig. 10 are conducted with Raman spectroscopy (Horiba Jobin Yvon LabRAM Aramis) with excitation wavelength of 442 nm, power of 0.01 \( mW \) and spot size of 1 \( \mu m \).

XPS (Thermo Scientific K-Alpha) is performed with spot size of 30 \( \mu m \) and energy resolution of 0.57 eV. LEEM and LEED (SPECS Fe-LEEM/PEEM P90) are conducted with incident electron energies of 25 eV and between 19–135 eV, respectively. STM and STS (Omicron VT, base pressure of \( 10^{-12} \) mbar) are performed simultaneously at 300 K using electrochemically etched W tips. STS data is generated by superimposing a 30 mV modulation at 10 kHz on top of the bias voltage and analysing the tunnelling current with a SR830 Lock-In Amplifier. XRR measurements (Bruker D8 Discover with a VANTAGE 500 Area Detector) are performed with a Cu K\(_{\alpha}\) X-ray source.

**Device fabrication.** The nanoribbons are transferred onto SiO\(_2\)/Si wafers as described, above. Electron-beam lithography is used to define source and drain electrodes with channel lengths between 75 and 220 \( nm \). Thermal evaporation is used to deposit Pd electrodes 35 \( nm \) in thickness. The back-gate electrode and back-gate dielectric are the Si wafer and 15 \( nm \) of thermally grown SiO\(_2\), respectively. Each field-effect transistors (34 m) is measured at room temperature in ambient conditions using a source voltage of \( \sim 0.1 \) V.

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