A wide-bandgap metal-semiconductor-metal nanostructure made entirely from graphene

J. Hicks¹, A. Tejeda², A. Taleb-Ibrahimi⁴, M. S. Nevius¹, F. Wang¹, K. Shepperd¹, J. Palmer¹, F. Bertran³, P. Le Fèvre³, J. Kunc¹, W. A. de Heer¹, C. Berger¹,⁵ and E. H. Conrad¹*¹

Present methods for producing semiconducting-metallic graphene networks suffer from stringent lithographic demands, process-induced disorder in the graphene, and scalability issues. Here we demonstrate a one-dimensional metallic-semiconducting-metallic junction made entirely from graphene. Our technique takes advantage of the inherent, atomically ordered, substrate–graphene interaction when graphene is grown on SiC, in this case patterned SiC steps, and does not rely on chemical functionalization or finite-size patterning. This scalable bottom-up approach allows us to produce a semiconducting graphene strip whose width is precisely defined to within a few graphene lattice constants, a level of precision beyond modern lithographic limits, and which is robust enough that there is little variation in the electronic band structure across thousands of ribbons. The semiconducting graphene has a topographically defined few-nanometre-wide region with an energy gap greater than 0.5 eV in an otherwise continuous metallic graphene sheet.

Patterning a flat graphene sheet to alter its electronic structure was expected to be the foundation of graphene electronics¹. The early focus was to open a finite-size gap in lithographically patterned nanoribbons, a necessary step for digital electronics²–⁵. Although early transport measurements supported this possibility⁶, it soon became apparent that these transport gaps originated from a series of mismatched-level quantum dots caused by the inability of present lithography techniques to produce sufficiently narrow, well-ordered and crystallographically defined graphene edges⁷–¹⁰. A working solution to the gap problem has yet to be formulated, let alone demonstrated. We show that such a solution exists, not by patterning, but instead by controlling the graphene–substrate geometry.

We have been able to construct a unique, reproducible and scalable semiconducting graphene ribbon with a ≥0.5 eV gap. Using pre-patterned SiC trenches to force graphene to bend between a (0001) face and a low-symmetry facet, we produce a narrow graphene ribbon with localized strain. This topographically defined ribbon is a wide-gap semiconductor a few nanometres wide that extends hundreds of micrometres. The strip connects seamlessly to metallic graphene sheets on both of its sides. From this simple morphology, we have not only produced a gap suitable for room-temperature electronics, but we have also demonstrated how narrow Schottky barriers can be fabricated in a scalable architecture.

Nanopatterned graphene ribbon arrays

Here, we present studies on how graphene’s band structure is altered when it is bent over steps. The bending causes both a local strain and a change in the sp² bond angle. In addition, local charging produces a Coulomb gradient across the bend. Both the local strain and the Coulomb potential confine the electron wavefunction in the bend. This confinement in turn depends on how the defining boundary is oriented relative to two inequivalent graphene directions: the (010)G zigzag direction and the (110)G armchair direction¹¹–¹². For example, graphene ribbons with armchair edges are predicted to open a gap whereas zigzag edges should not¹¹–¹⁴. It is therefore critical that graphene is bent along graphene’s (110)G armchair direction (Fig. 1a).

To do this, we use epitaxial graphene grown on SiC(0001). Epitaxial graphene is known to flow over random intrinsic nanometre-tall SiC steps¹⁵–¹⁶. Instead of random steps, we use large arrays of pre-patterned parallel steps in SiC to make angle-resolved photoemission spectroscopy (ARPES) measurements possible. This can be done with epitaxial graphene because, unlike all other graphene production methods, epitaxial graphene is both atomically flat and epitaxially oriented with respect to the SiC substrate. Furthermore, epitaxial graphene grown on the (0001) surface is always rotated 30° from the SiC (1010)SiC direction¹⁵. This epitaxy means the armchair edge of growing graphene can be aligned parallel with patterned SiC trenches if they run perpendicular to the SiC (1100)SiC direction (Fig. 1a,b,d). Details of the production method are given in refs 17,18. The trench walls are initially vertical, but facet into a few stable crystallographic planes during graphene growth (explained in more detail in the next section).

The growth conditions were set to produce a single graphene layer above the buffer graphene-like sheet on the SiC(0001) (ref. 18). Both layers grow over the trench edge onto the sidewall facet¹⁶. Figure 1d shows a schematic of the ribbon geometry. An example of the post-graphitized arrays is shown in Fig. 1b,c. The ribbons are extremely straight over micrometres with a trench-height r.m.s. roughness of less than one 4H–SiC unit cell (1 nm). For a typical trench pitch of 100 nm, the ARPES beam (~50 μm in diameter) illuminates ~500 ribbons. If these ribbons are not sufficiently straight and parallel, the averaged ARPES signal will be degraded.

¹The Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA. ²Institut Jean Lamour, CNRS—Univ. de Nancy—UPV-Metz, 54506 Vandoeuvre les Nancy, France. ³Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin, 91192 GIF sur Yvette, France. ⁴URI CNRS/Synchrotron SOLEIL, Saint-Aubin, 91192 GIF sur Yvette, France. ⁵CNRS/Institut Néel, BP166, 38042 Grenoble, France. *e-mail: edward.conrad@physics.gatech.edu.
To understand how the ARPES spectrum would look from a curved graphene, the CNT is periodic in $\theta$ (that is, $a_{\parallel}$ is a valid quantum number). Therefore, the CNT’s dispersion is manifestly one-dimensional (1D) semiconductor, as we will now show.

The most important feature in Fig. 2a is that the transition region, $\theta = -35^\circ \leq \theta \leq -20^\circ$, between the (0001) and the facets. In this angular range, graphene’s band structure markedly switches from discrete Dirac cones to a continuous distribution (in $\theta$) of broad diffuse cones. An example cone is shown in Fig. 2c. It is clear that this cone has an energy gap and a significantly lower slope (velocity $\propto dE/dk_y$) than that measured for either the (0001) or the facet surfaces. Figure 3a compares an energy distribution curve (EDC; intensity versus energy at a constant $k_x$) and the $\Theta$-point for a transition cone and the (2207) facet cone. The spectral density for the transition cone decays rapidly below the valance band edge, $E_v \sim -0.5$ eV. This is not a doping shift because there are no π bands above $-0.5$ eV. As the position of $E_F$ in the gap is not known, the lower limit on the gap size is 0.5 eV. This gapped region is a manifestation of a nearly one-dimensional (1D) semiconductor, as we will now show.

Junction potential boundary

The gapped graphene region is unique because it represents a nearly 1D graphene semiconductor seamlessly connected to two 2D graphene sheets on its sides. To demonstrate this, one must first understand how the ARPES spectrum would look from a perfect 1D system: a rolled-up graphene sheet; that is, a carbon nanotube (CNT). If we align an infinite CNT with its axis along the same $\gamma$ as our bent graphene, the CNT is periodic in $\theta$ (that is, $a_{\parallel}$ is a valid quantum number) and $\theta$, (that is, $a_{\parallel}$ is not a valid quantum number). Therefore, the CNT’s dispersion is completely defined by $a_{\parallel}$ and a subband index, $n$, related to the $\theta$ periodicity, $E_s(k_z)$. As the dispersion is independent of $a_{\parallel}$, there is no change in the ARPES $E(k_z)$ dispersion when the CNT is rotated by $\theta$. If we consider the bent graphene region as a partial arc of a CNT, then an ARPES measured $E(k_z)$ should also be independent of $\theta$.

Like the CNT example, the bent graphene is rotated around an axis parallel to the $y$ axis (along the step edge) so $E(k_x)$ for the curved graphene should be nearly independent of $k_x$, $\theta$; that is, $E_x(k_z)$ should be independent of $\theta$. To demonstrate this, we have plotted $E_x(k_z)$ for two values of $\theta$ within the transition region (Fig. 3c,d). The dispersion is nearly identical even though the 3° angular separation represents a $\Delta k_z \sim 8$% of the Brillouin zone. This is more clearly shown in Fig. 3e where we plot EDCs $(|I(E)|/|E_n|)$ for all angles measured in the transition region. These plots show that $E_y(k_z)$ is independent of $\theta$ over a 12° range. This simple experiment

**Figure 1** The experimental geometry of measuring graphene on SiC trenches. a The graphene Brillouin zone orientation relative to armchair edge ribbons. b AFM top view of sidewall ribbons showing their long-range order. c Perspective AFM view of 18-nm-deep graphitized trenches. d Schematic side view of the sidewall ribbons containing two structural graphene sheets (the lower sheet in red is referred to as the buffer layer). Grey regions are curved semiconducting parts of the graphene. The schematic shows the detector orientation to reach both the K-point of the flat surface and the facet with normal $\hat{n}_i$. Sample $k_y$ and constant $E$ cuts are shown through the Dirac cones of the (0001) and facet surfaces.

**Topographical band structure changes**

To use ARPES, we orient the patterned SiC step edges with the $\theta$ rotation axis of the sample as shown in Fig. 1d. The $\gamma$ direction is parallel to the step edge (the $\theta$ and $k_x$ axes are co-planar). This orients the graphene Brillouin zone relative to $k_x$, as shown in Fig. 1a. Photoelectrons from a surface with a local normal $\hat{n}$ have momentum $k$ and $k_y(\theta - \Delta \theta)$, where $k_y(\theta - \Delta \theta)$ is in the plane of the local facet. The ARPES detector measures $E(k_y)$ ($k_x$ ⊥ to $\hat{r}$). Rotating $\theta$ is equivalent to scanning $E(k)$ along $k_y(\theta - \Delta \theta)$ (0 sorter direction).

To reach the graphene K-point of the (0001) surface ($\hat{k}_y = (1.704\mu$m$)^{-1}$), the sample must be rotated by $\theta_0 = \sin^{-1}(K_y(2m\hbar^2)^{-1/2}(h_0 - \Phi)^{-1/2})$, which is $\pm 37^\circ$ for the photon energy, $h_0$, and work function, $\Phi$, used in this experiment. Placing the detector at this $\theta$ will produce an $E(k_y)$ cut through the Dirac point of the Dirac cone. The Brillouin zone of the sidewall graphene is tilted by $\Delta \theta$ of the facet normal. This means that the K-point for that facet graphene will be at $\theta_i = \theta_0 \pm \Delta \theta_i$. By scanning $\theta_i$, facet normals can be identified each time a Dirac cone is measured in the detector. Figure 2a shows a $\theta$ scan at constant energy from a 12-nm-deep trench array. There is no intensity and therefore no cones between $-36^\circ$ to $-33^\circ$ and $-20^\circ$ to $-12^\circ$, indicating there are no stable facets in this range. There are four regions where cones do appear. Figure 2b–e shows the ARPES measured cones from these regions. The K-point Dirac cone at $\theta_i = -37^\circ$ is from the (0001) surface (Fig. 2b). This is the typical band structure of a single graphene sheet above the buffer $^{15}$, the top layer is n-doped by $E_0 - E_F = -0.43$ eV, where $E_0$ and $E_F$ are the Dirac and Fermi energies respectively, typical of clean, ordered (0001) epitaxial graphene $^{19}$.

At small $\theta$ there are two sets of two Dirac cones with $\theta_i = \pm 9^\circ$ and $\pm 4.5^\circ$. These cones are from graphene grown on (2207), and (1103) facets on one trench side and their complementary (2207), and (1103) facets on the opposing trench. The facet Dirac cones are slightly p-doped as discussed later. The sidewall graphene on these facets is extremely well ordered. Significant disorder would lead to a $\Delta k_y$ broadening above the instrument resolution, $\Delta k_y (0.04\mu$m$)^{-1}$). Along the step edge direction, the $\Delta k_y$ broadening is not measurable for 36-nm-wide ribbons. However, $\Delta k_y \sim 0.08\mu$m$^{-1}$ is observed for 15-nm-wide ribbons. Atomic force microscopy (AFM) shows that most of this disorder is due to local surface normal variations, $\Delta \Phi (\Delta \Phi \sim \Delta k_y/k_x \sim 2^\circ)$. Similarly, the $\Delta k_y$ broadening is due to surface normal variations in $\theta$ ($\Delta \theta \sim 1.6^\circ$). Keeping in mind that these ARPES widths are an average over >500 parallel ribbons (each 50μm long), the facet orientation is exceptionally high.
demonstrates that the gapped graphene is confined to a very narrow, nearly 1D region of the film.

Unlike the CNT, the bent graphene is a finite width strip. This means that the ARPES signal is not completely independent of \( \theta \). The measured intensity is modulated by a \( \theta \)-dependent envelope function due to the diffraction limit broadening of 30 eV photoelectrons (\( \lambda = 0.22 \text{ nm} \)) from a source with dimension \( D \). The envelope can be used to estimate the coherent dimension of the bend. Figure 3b shows the relative intensity of the transition cones versus \( \theta \). A fit of the measured \( I(\theta) \) to the broadening function \( \text{sinc}^2(\pi D\sin\theta / \lambda) \) gives \( D = 1.4 \text{ nm} \). This width is consistent with the bend radius observed in electron microscopy measurements\(^{16}\).

Of course, the bent graphene band structure cannot be fully understood in the context of a CNT because the wavefunction boundary conditions are different in the two systems. Instead of CNT’s cyclical boundary conditions, the bent graphene is an arc that is bounded by two flat graphene sheets on both sides, each with different doping. Although a self-consistent theory needs to developed, there are important effects that can influence the band structure of this system: strain, finite size effects, local Coulomb potential and substrate bonding.

Whereas strained bilayer graphene can lead to small gaps\(^{14,20,21}\), strain and electronic energies in bent graphene ribbons are comparably large. The strain associated with the observed \(~1\) nm radius of curvature can be very large\(^{16}\), and could produce bandgaps ranging from 0.2 to 0.5 eV depending on the model\(^{13,22,23}\). Comparing this strain energy with the confinement bandgap expected for a 1.4 nm ribbon, \( E_g \sim 1 \text{ eV-nm/}1.4 \text{ nm} = 0.7 \text{ eV} \) (refs 5, 24), shows that both effects lead to gaps similar to the experimental value. As strain and confinement energies are similar, a Peierls-like distortion is possible.

Besides the effect of strain and boundary conditions, there is an on-site potential at the bend caused by the different doping on either side of the ribbon. The charge distribution at the metal–semiconducting boundary, and the associated Schottky barrier, will require a self-consistent solution. As the Schottky barrier is so narrow, the exact boundary condition will be important in determining tunnelling resonant states that can influence transport through the metal–semiconductor–metal region. Evidence for this has been reported in graphene conductivity measurements over randomly oriented 1 nm SiC steps\(^{25}\). Although graphene’s strain going over a 1 nm step should be significantly smaller than the taller steps studied in this work, the transport findings in ref. 25 are consistent with a semiconducting strip at the step.

Although a good theoretical understanding of the electronic structure remains to be formulated, we have used a simple tight-binding calculation that reproduces many of the salient features of the ARPES data (see Supplementary Information). The model consists of a 2,000-atom-wide flat graphene sheet. A 1.5 nm strip in the middle of the film has a different hopping integral to mimic the effect of strain at the bend\(^{13,26,28}\). In addition, a position-dependent on-site potential is used to account for the n- to p-doping transition (detailed below and in the Supplementary Information). The calculated \( E(k_y) \) is shown in Fig. 2b,c,e. Note that the model produces a significant number of states within the semiconducting cones. This correlates well with the experimental diffuse intensity within the cone.

### Facet band structure

As the bend boundary conditions are critical to understanding the ribbon band structure, it is worth looking at the differences between graphene grown on the (0001) surface and sidewall facets.
Figure 3 | Different views of the nearly 1D gap semiconducting bent graphene. 

Graphene on the (0001) surface is metallic and n-doped whereas sidewall graphene has a small p-doping. Figure 4a shows that the (1103) facet has a $\sim 70$ meV p-doping. It is difficult to say with certainty whether or not the facet graphene may be semiconducting because the doping is comparable to the maximum expected gap (that is, for $W = 15$ nm ribbon, $E_g \sim 66$ meV; ref. 24). All ribbons, regardless of width, show the same shape near $E_g$ as demonstrated in Fig. 4b.
A close-up electrostatic force microscope image of the ribbons in Fig. 5a shows a contrast change on the sidewalls. This is correlated with a Raman 2D peak once graphene has formed but can also be due to a work function change. Indeed, there is a \( \approx 1.5 \text{ eV} \) decrease in the facet work function measured from the photoelectron secondary electron cutoff. Furthermore, as shown in Fig. 5b,c, a surface-derived set of bands near the K-point of the (0001) surface both shift to higher binding energy and change shape on the facet. Such differences are to be expected because the surface reconstruction must be different on the two facets. Low-energy electron diffraction shows that the \((6\sqrt{3} \times 6\sqrt{3})\tilde{R}30^\circ\) reconstruction spots of the (0001) face disappear on the facet walls (see Supplementary Information). The different surface symmetry implies that polarizability, bond re-hybridization, chemical reactivity and so on can all be different and lead to charge transfer that could explain the different observed dopings.

One last point must be mentioned. The bilayer graphene pair on the facets must have a large relative slip between layers (\( \approx 30\% \) of the graphene unit cell assuming a 1 nm bend radius over a \( 29^\circ \) arc). It has recently been shown that sliding graphene layers can significantly distort the K-point band structure\(^3\). This may explain why the experimental two-layer Dirac cones are similar to those from a single graphene sheet.

**Conclusion**

We have shown that a nearly 1D, large-bandgap, semiconducting graphene ribbon, seamlessly connected to metallic graphene sheets, can be produced from a scalable bottom-up approach by forcing topographical changes in the SiC that in return affect graphene’s electronic properties. The ribbons produced this way have a bandgap energy \( \geq 0.5 \text{ eV} \) and are both narrow (\( \approx 1.4 \text{ nm} \)) and continuous over macroscopic lengths. In a sense, the macroscopic arrays of graphene metallic-semiconducting junctions in this work are the ideal architecture predicted for CNT electronics; perfectly aligned ribbons with identical chirality patterned over macroscopic distances with atomic precision. The rough edge problem associated with lithographic patterning is solved using a bottom-up assembly as the graphene grows\(^7\). The edges in this work are atomically perfect because they are simply a curved distortion, defined by potential gradients (elastic or electronic), in a continuous graphene sheet.

Here, we not only show the importance of the graphene-substrate interaction, but we also demonstrate how the support substrate can be used to purposely alter graphene’s electronic properties. We give an important example of how a well-ordered, commensurate substrate interaction can be used to force topographical changes in the graphene that lead to metal–semiconducting transitions and alter its doping. The large number of ways the substrate can be altered means that new ways of approaching scalable geometry-dependent devices will be forthcoming. Exploring the transport properties of the junctions described in this work is just...
beginning. New architectures based on the principles outlined here are sure to significantly alter graphene electronics research.

**Methods**

The substrates used in these studies were n-doped at $2 \times 10^{19}$ cm$^{-2}$ 4H-SiC. The graphene ribbon arrays were made by a selective growth method. Vertical trenches were first produced on the SiC(0001) surface and then graphitized in a controlled silicon sublimation furnace. The arrays were prepared by first producing a negative HSQ mask by electron-beam lithography. The SiC substrate was reactive ion etched with a SF$_6$–O$_2$–Ar plasma to produce trenches of 7.5–18 nm in depth depending on the etching time. The samples were graphitized by heating to 1,560 °C in a carbon radiofrequency furnace. The parallel trench arrays were made with a pitch between 100 and 400 nm over a 1 × 3 mm$^2$ area (2,500–10,000 1-mm-long trenches).

The samples were transported in air before introduction into the ultrahigh-vacuum analysis chamber. Before ARPES measurements the graphene films were thermally annealed at 800 °C in ultrahigh vacuum. ARPES measurements were carried out at the Cassiopée beamline at the SOLEIL synchrotron with a high-resolution modified Pettersen grating monochromator with a resolution $E/\Delta E \approx 25,000$ below 100 eV. The detector is a Scienta R4000 detector with resolution $\Delta E < 1$ meV and $\Delta k \sim 0.03$ Å$^{-1}$ at $h\nu = 36$ eV. All measurements were carried out at 100 K. The total measured instrument resolution is ($\Delta E < 12$ meV).

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**Author contributions**

E.H.C. supervised the project, designed and carried out the experiment, analysed data and wrote the manuscript. J.H. and A.T. carried out the experiment, analysed data and edited the manuscript. A.T-I. organized the ARPES experiments and recorded the data. C.B. and M.S.N. carried out the experiment and the manuscript. K.S., F.B. and P.L.F. helped run the ARPES experiments. F.W. analysed the data and edited the manuscript. W.A.d.H. and J.K. provided the theoretical band modelling and edited the paper.

**Additional information**

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to E.H.C.

**Competing financial interests**

The authors declare no competing financial interests.