Supplementary Information for Solution-Synthesized Chevron Graphene Nanoribbons Exfoliated onto H:Si(100)

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The supplementary information provides additional analysis of chevron GNRs on H:Si(100) including height distributions, manipulation of GNRs with the STM probe, DFT modeling results, and scanning tunneling spectroscopy data.
Figure S1. (a-c) STM images showing 64 graphene nanoribbons with solid lines indicating the nanoribbon longitudinal axis directions. When the longitudinal axis of the graphene nanoribbon is parallel to the silicon dimer row direction, the relative angle is 0 degrees, and when the longitudinal axis of the graphene nanoribbon is perpendicular to the dimer row direction, the relative angle is 90 degrees. (d) Histogram showing the measured orientations of chevron GNRs relative to the silicon dimer rows. Although fewer ribbons were found oriented at 45 degrees relative to the dimer row direction, no claims are made about GNR-substrate alignment because the motion of the applicator is not well-controlled and may play a role in causing the GNRs to align to a particular orientation. (e) Additional STM topograph showing several graphene nanoribbons with correlated orientations. The movement of the applicator may align the GNRs on the surface independently of substrate-GNR interactions.
Figure S2. Heights of chevron graphene nanoribbons on H:Si(100) (a-d) Height distributions of semitransparent graphene nanoribbons showing a height of 1.84 – 2.56 Å (e-h) STM topographs with white rectangles indicating regions used to generate height distributions in (a-d). (i-k) Height distributions for nontransparent graphene nanoribbons, showing heights of 3.24 Å – 3.57 Å. (l-n) Topographs used to generate the height maps in i-k. These ribbons do not show semitransparency, and several GNRs are simultaneously examined. To determine the heights of graphene nanoribbons, a portion of the image is selected, and the heights at each point are plotted. The GNR height is determined as the difference between the substrate and GNR peak centers. In some cases the peak position is determined using a Gaussian fit, as illustrated above, but in many cases the peak position is estimated. The box is chosen to capture the entire GNR, or the portion on the same terrace as the surrounding substrate. Images with artifacts or where the substrate near the GNR is not clearly imaged are excluded. The topographs used to generate Figure 1f in the main text include STM images collected at +2V, -2V, and -1.5V. The tunneling current ranges from 10 pA to 1000 nA, with most of the data collected at 10 or 100 pA. The height difference observed is greater than what has been previously seen for semitransparent graphene, possibly due to the narrow lateral dimensions and nanowiggles of the GNR enabling additional pliability. The height distribution for a nanoribbon that shows both semitransparency and nontransparency is shown in (a) and the corresponding topograph is shown in (e). There is a 1.5 Å height difference between the semitransparent and nontransparent portion of the same nanoribbon. In this case there is no evidence of a change in the configuration of the probe, so the semitransparency may be influenced by buckling of the nanoribbon, which depends on a lattice mismatch between graphene and the H:Si(100)2x1 surface or defects on the substrate.
Figure S3. (a-b) STM topographs of graphene nanoribbons on H:Si(100). Sample bias: -2V; tunneling current: 10 pA. In (a) the lower graphene nanoribbon appears non-transparent. In (b) the same graphene nanoribbon appears semi-transparent, with the corrugation of the silicon dimer rows visible underneath the graphene nanoribbon. The STM images shown in (a) and (b) demonstrate that the same nanoribbon can exhibit both semi-transparency and non-transparency. A previous study determined that the tip pushing the GNR closer to the surface can cause the semi-transparency effect. The dashed lines indicate positions where scanning tunneling spectroscopy was collected (c-d) Normalized dI/dV spectra maps collected along dashed lines indicated in (a,b). The positions of the silicon and GNR valence and conduction band edges are indicated by dashed lines. The bandgap of the GNR is comparable in both cases.
The scanning tunneling microscope was used to change the position and orientation of graphene nanoribbons. A graphene nanoribbon before and after nanomanipulation. Sample bias: -2V; tunneling current: 10 pA. Scale bar is 10 nm (a) Graphene nanoribbon on H:Si(100) surface (b) The tip is moved 4 Å closer to the surface and moved from left to right along the indicated white arrow. The feedback loop is off and the sample bias is held at -2 V. The ribbon is rotated by 80° and translated several nanometers. The weak interaction between the H:Si(100) surface and GNRs allows the nanoribbons to be pushed with the STM probe. The STM tip traces a height contour obtained from a previously collected topograph. As the tip travels along its predefined path, the tip is displaced an additional 5-9 Å closer to the surface. The sample bias is typically held at 0 V while the feedback loop is turned off.

Projected density of states for a six-unit cell GNR. Inset shows the structure of the modeled GNR. No substrate is included. States 1-8 are labeled and mapped onto spatial coordinates in Figures S6. In the main text, 2 valence states and 2 conduction states were indicated in Figure 2e and the corresponding normalized LDOS at 4 Å above GNR plane were calculated and compared with the normalized dI/dV images from experiments. Here more states near the Fermi level are indicated and the corresponding normalized LDOS at different heights above GNR plane are shown. Figure S6 shows the DFT calculated PDOS of the isolated 6-monomer GNR with the states marked out using indices from 1 to 8. The PDOS from DFT shows the bandgap to be ~1.6 eV, which is much smaller than the true quasi-particle bandgap of ~3.6 eV.
Figure S6. Simulated local density of states of a six-unit cell chevron GNR is plotted at heights of 4 Å to 1 Å above the GNR plane. The color range is set to be [0.1, 0.9] to more clearly reveal the features.
Figure S7. In the main text the experimental results show the influence of the silicon substrate on the GNR. Here simulations are performed to show the change of the GNR LDOS once it is placed on the H:Si(100) substrate. Periodic boundary conditions are applied to obtain the PDOS for an infinite GNR on H:Si(100). (a) Model showing chevron GNR on H:Si(100) slab. The atomic structure is shown with 16 layers of silicon included in the substrate to capture the bulk silicon bandgap. (b) Cross-sectional view showing the atomic structure and normalized charge distribution of GNR relaxed on the H:Si(100) surface. (c) PDOS plot of GNR and H:Si(100). The silicon slab has a Kohn-Sham bandgap of ~1.2 eV, which is the same of its bulk value.
Figure S8. Simulated local density of states (LDOS) for an infinite chevron GNR on H:Si(100) plotted at heights from 4 to 1 Å above the GNR plane. The states are chosen at energies corresponding to peaks of the GNR PDOS and the corresponding normalized LDOS at different heights above GNR plane are shown. Since the bandgap of the silicon substrate is smaller than that of the GNR on top, some features seen in the normalized LDOS within the bandgap of the GNR (State 5 and State 6) are caused by the LDOS of silicon. For other states, there are small signatures shown in the normalized LDOS of GNR, which are also attributed to silicon DOS.
Figure S9. Density of states maps used to determine GNR bandgaps. (a-c) STM topographs of graphene nanoribbons on H:Si(100). Scalebars are 5 nm. The dashed lines indicate positions where variable spacing I-V spectroscopy was collected (d-f) Normalized $dI/dV$ spectra maps across GNRs. The positions of the GNR valance and conduction band edges are indicated by dashed lines. (g-i) Normalized $dI/dV$ plots showing data used to generate the maps shown in d-f. The GNR and Si bandgaps are indicated. (j) Histogram plotting the bandgaps of 21 GNRs measured. The average bandgap is found to be $2.85 \pm 0.13$ eV.
Figure S10. (a) Normalized $dI/dV$ spectroscopy collected from GNR center, GNR edge, and the silicon substrate. The positions of the Si VB and CB are indicated. (b) Normalized $dI/dV$ maps at sample biases corresponding to the energies of the silicon states. The GNRs appear darker than the surrounding silicon due to their decreased density of states. There is a modulation of the density of states collected over the GNRs that is commensurate with the silicon lattice, supporting the claim of substrate contribution to the spectroscopy measurement.

REFERENCES
