

## Supporting Information for

# How Graphene Islands Are Unidirectionally Aligned on the Ge(110) surface

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## Methods

**Graphene synthesis.** The Ge(110) substrates (500  $\mu\text{m}$  thick, AXT) were cut into  $1 \times 1 \text{ cm}^2$  pieces and placed in a 2-inch horizontal quartz tube. The quartz tube was evacuated to approximately  $10^{-4}$  mbar and then filled with 200 standard cubic cm per min (sccm) argon (Ar, 99.9999% purity) and hydrogen ( $\text{H}_2$ , 99.9999% purity). To synthesize the graphene islands with adequate density,  $\text{H}_2$  gas flow rate of 25 sccm was chosen for pre-annealed Ge substrate (flat surface). While, for graphene grown on Ge substrate with type 1, type 2 and type 3 atomic steps (rough surface),  $\text{H}_2$  gas flow rates were selected as 30 sccm, 30 sccm and 27 sccm, respectively. Then the quartz tube was heated to 910  $^\circ\text{C}$  for 30 min and 0.5 sccm methane ( $\text{CH}_4$ , 99.99%) was introduced to deposit the graphene film for different durations (from 60 min to 200 min). Afterwards, the  $\text{CH}_4$  gas was turned off and the furnace was cooled to room temperature under flowing  $\text{H}_2$  and Ar. The step-terrace structure was primarily determined by the unavoidable cutting misalignments with respect to the (110) plane when the crystal surfaces were prepared,<sup>1</sup> and it was found that the atomic step density on Ge(110) surface was relatively stable at the growth temperature of 910  $^\circ\text{C}$ , but decreased with the increase of temperature. When the annealing temperature approached to the melting point of Ge (938.3  $^\circ\text{C}$ ), the atomic steps on the Ge(110) surface were dramatically reduced. In order to reduce the density of the atomic steps, the Ge(110) substrate was intentionally pre-annealed at 937  $^\circ\text{C}$  (close to the melting point of Ge) for at least 30 min under flowing  $\text{H}_2$  and Ar.

**Characterization.** The topological images of graphene were obtained by the AFM (Multimode 8,

Bruker) in the tapping mode using RTESP AFM tips. Raman spectroscopy (HORIBA Jobin Yvon HR800) was performed using an  $\text{Ar}^+$  laser with a wavelength of 514 nm and a spot size of 1  $\mu\text{m}$ . Scanning tunneling microscopy (SPECS JT-STM) was performed in an ultrahigh vacuum (UHV) chamber with a base pressure below  $8 \times 10^{-11}$  mbar at 4.3 K. The STM measurements were taken in the constant current mode by applying a bias voltage to the sample. The LEED measurements were conducted on a 6-inch LEED apparatus (ErLEED 100, SPECS GmbH) in ultrahigh vacuum (base pressure  $< 5 \times 10^{-8}$  Pa). The electron beam energy was set to 130 eV for all the samples and the diameter of the electron beam was  $\sim 1$  mm.

**Computational details.** The calculation was performed within the framework of DFT as implemented in the Vienna Ab initio Simulation Package (VASP). The electronic exchange and correlation were included through the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form. The interaction between valence electrons and ion cores was described by the projected augmented wave (PAW) method and the energy cutoff for the plane wave functions was 400 eV. The van der Waals interaction was considered by using DFT-D<sub>2</sub> and the spin-polarized calculation was performed for dangling bonds on the graphene edge. All the structures were optimized until the maximum force component on each atom was less than 0.02 eV/Å. The vacuum layer inside the super-cell was kept as large as 15 Å to avoid the interaction between adjacent unit cells. For a supercell larger than 15 Å  $\times$  15 Å  $\times$  15 Å, the Brillouin zone was sampled only by the G point, otherwise a 2  $\times$  1  $\times$  1 or 1  $\times$  5  $\times$  1 k-point mesh was used. The substrate was modeled as a periodic slab consisting of at least five atomic layers and

the bottom two layers were fixed to mimic the bulk. Restricted by the calculation size, the substrate lattice was stretched or compressed slightly ( $< 4\%$ ) to build a co-periodic lattice for graphene and substrate. The Ge atoms on the top and bottom layers were passivated by H atoms.

### Phase diagram calculation

The optimized geometries and formation energies of hydrogen and germanium passivated graphene nanoribbons with armchair (AC-GNR) edges on the flat and stepped Ge(110) surfaces (shown in Figure 4) were calculated. A  $[-110]$  oriented step was chosen as a typical atomic step on the Ge(110) surface. The H terminated AC-GNR was put on the substrate with the armchair edge along the  $[-110]$  direction of the Ge(110) surface. By interacting with the H-passivated Ge(110) surface, some of the H atoms in the graphene edge would react with the H atoms on the substrate and were desorbed as  $H_2$ . To compare the stability of the four structures, we defined the formation energy,  $E_f$ , of each structure as:

$$E_f = (E_{(tot)} + 0.5\Delta n \times E_{(H_2)} - E_{(sub)} - E_{(GNR-H)}) / L \quad (1)$$

where the  $E_{(tot)}$  are the energies of the four structures shown in Figure 4,  $E_{(H_2)}$  is the energy of hydrogen molecule,  $E_{(sub)}$  and  $E_{(GNR-H)}$  are the energies of Ge(110) substrate and H-terminated graphene nanoribbons (GNR-H), respectively,  $\Delta n$  is the number of  $H_2$  molecule dehydrogenated from C-Ge bond formation, and  $L$  is the length of supercell along the periodic direction. The two structures on the left panel of Figure 4 represent the hydrogen-passivated graphene (H-Gr) edge and germanium-passivated graphene (Ge-Gr) edge on the flat terrace of the Ge(110) surface and

the structures with the H-Gr and Ge-Gr edges near the  $[-110]$  oriented step of the Ge(110) surface are shown in the right panel of Figure 4.

To obtain the thermodynamic phase diagram of AC-GNR on the Ge(110) surface, it is essential to compare the free-energy difference  $\Delta G$  of AC-GNR with Ge-Gr and H-Gr structures.  $\Delta G$  can be calculated by:

$$\Delta G = \Delta E_f - N_H \times \mu_H(T, P) \quad (2)$$

where  $\Delta E_f$  is the difference in the formation energy (calculated by Eq. 1) between the H-Gr and the Ge-Gr edges,  $N_H$  is the number of H atoms, and  $\mu_H$  is the chemical potential of the  $H_2$  gas as a function of  $H_2$  partial pressure  $P$  and temperature  $T$ . By setting  $\Delta G = 0$ , we could obtain the thermodynamic diagram of graphene with the armchair edge on the Ge(110) surface with terraces or  $[-110]$  oriented steps as shown in Figure 4. Meanwhile, the similar thermodynamic diagram of graphene with the zigzag edge was obtained and shown in Supporting Information Figure S3.

### **Formation energy of the Ge-Gr interface**

Three typical surface steps were considered in our calculation:  $[-110]$  oriented step (S-I),  $[001]$  oriented step (S-II), and step with an arbitrary direction ( $76.74^\circ$  deviated from  $[-110]$  direction, S-III). The GNR with one edge terminated by H atoms and another bare edge attached to the atomic step of Ge(110) surface was put near the step edge and optimized. To explore the optimum bonding orientation of the graphene edge at each surface step, we calculated the

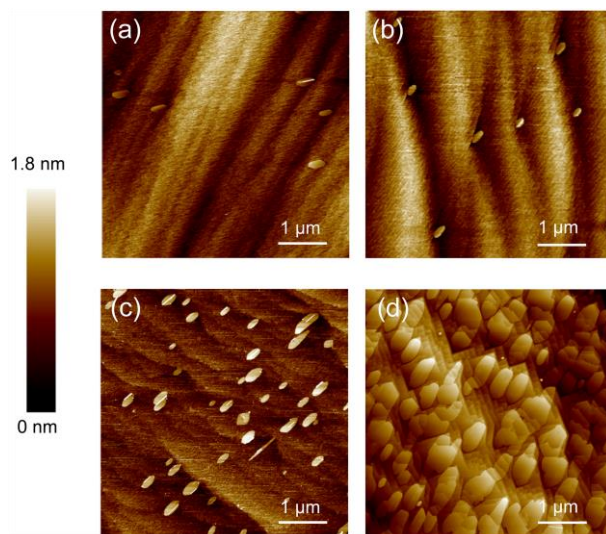
formation energies of the Ge-Gr edge with different  $\Delta\theta$  which was defined as the misorientation angle between the [-110] direction of the Ge(110) surface and the armchair direction of graphene.

The formation energy of Ge-Gr edge at the surface step was calculated as:

$$E_F = (E_{(tot)} - E_{(sub)} - E_{(GNR)} + E_{F(GNR)}) / L \quad (3)$$

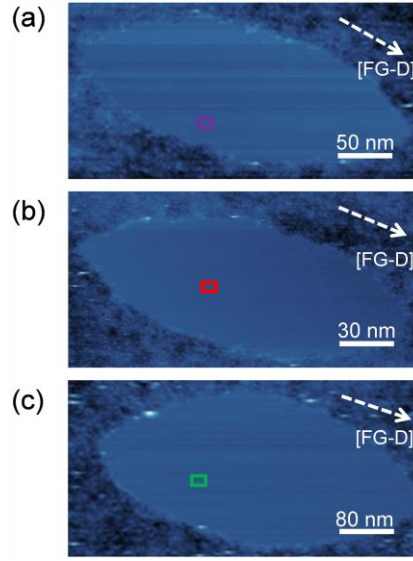
where  $E_{(tot)}$ ,  $E_{(sub)}$ , and  $E_{(GNR)}$  are the calculated energies of the Ge-Gr edge at the Ge(110) step, stepped Ge(110) substrate, and isolated GNR respectively,  $E_{F(GNR)}$  is the formation energy of GNR with a free edge, and  $L$  is the length of GNR. Owing to the  $C_6$  symmetry of graphene,  $\Delta\theta$  varies from 0 to 30 °.

Limited by the size of calculation model, five different  $\Delta\theta$  values were considered for each step. The optimized structures and formation energies are summarized in Supporting Information Figure S4. With regard to the Ge(110) surfaces with three typical atomic steps, the minimum formation energies are obtained at  $\Delta\theta = 0^\circ$ , suggesting that the armchair direction of the graphene island is always parallel to the [-110] direction of the Ge(110) surface regardless of the direction of atomic step on the Ge(110) surface.

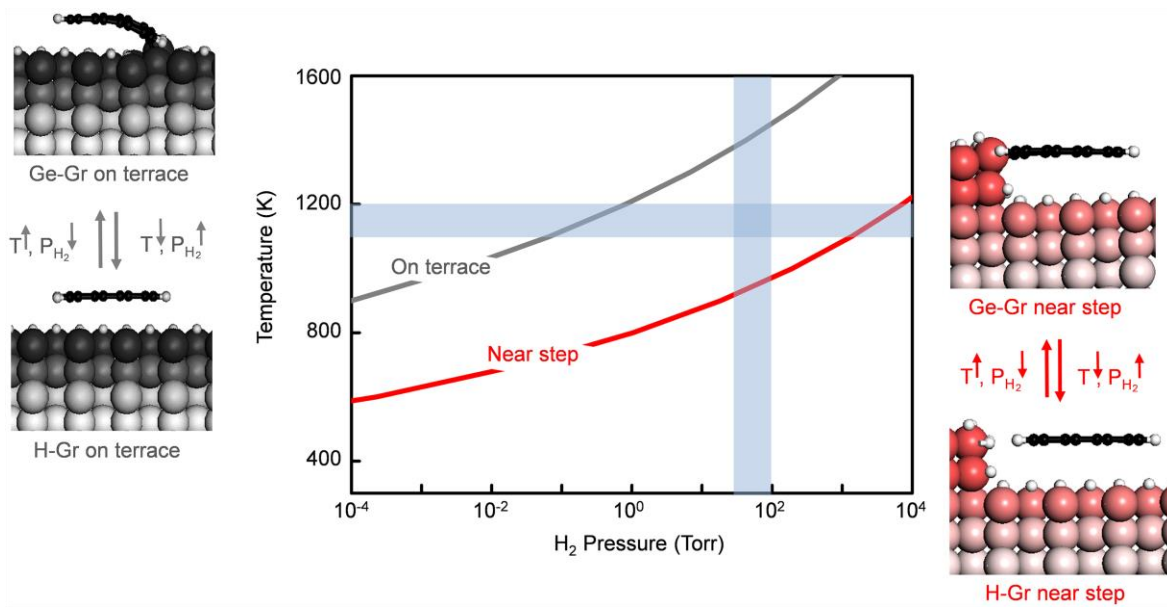


**Figure S1.** For the Ge(110) surface consisting of irregular atomic steps, the graphene islands are always unidirectionally aligned. Furthermore, all the aligned graphene islands are attached to the atomic steps of the substrate.

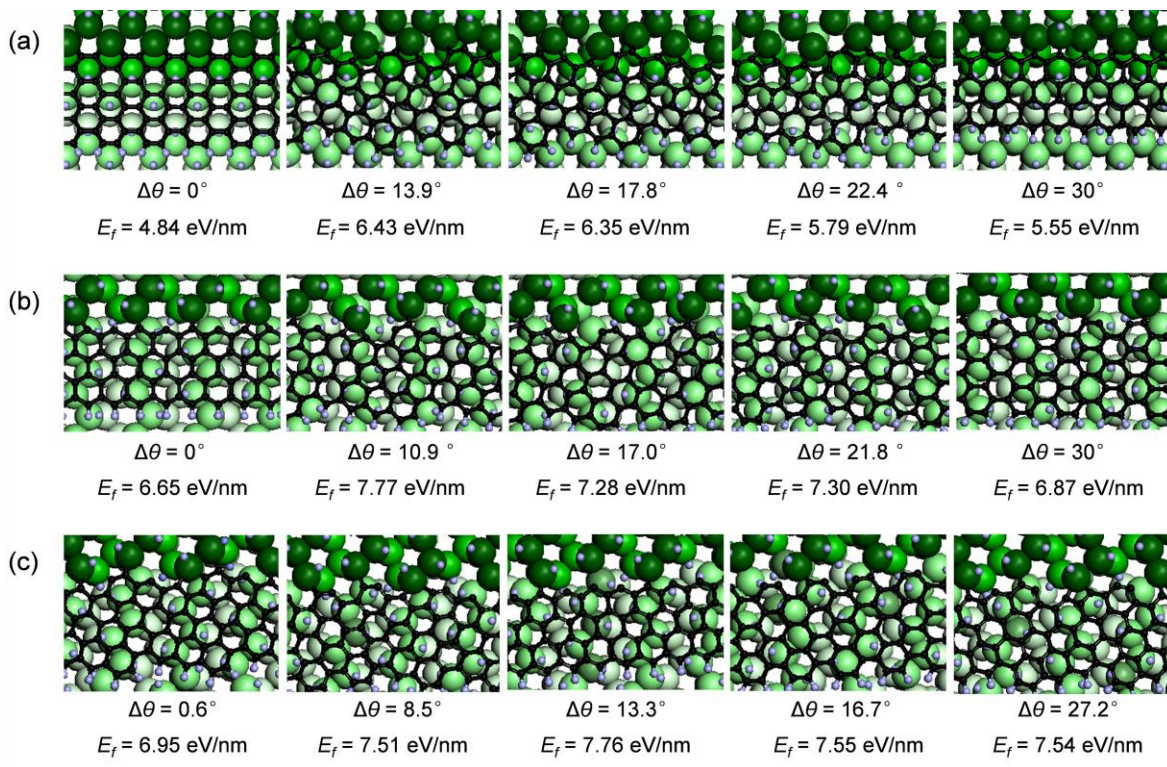




**Figure S2.** STM images ( $V = 2$  V) of the single graphene island near the three representative step edges. The dashed white arrows indicate FG-Ds. The tunneling currents are (a) 1.5 nA, (b) 0.06 nA and (c) 0.2 nA, respectively. The high-resolution STM images in Figure 3 are taken from the colored rectangles, respectively. By comparing the lattice images, it can be concluded that the FG-D of graphene island coincides with the  $[-110]$  direction of the Ge(110) substrate. Therefore, based on our STM images (Figure 3) and AFM images (Figure 1d,f), the atomic steps shown in Figure 1c,d and e,f are found to be  $[-110]$  oriented and  $[001]$  oriented, respectively.



**Figure S3.** Thermodynamic diagram of graphene with the zigzag edge on the Ge(110) surface with terraces or [100] oriented steps. Structures for hydrogen-passivated and Ge-passivated graphene with zigzag edge on the terrace are shown in the left panel and those with zigzag edge near the [001] oriented atomic step are shown in the right panel. The hydrogen-passivated edge will be transformed into Ge-passivated one with the increase of temperature and decrease of  $H_2$  pressure, and vice versa.



**Figure S4.** (a) Optimized structures and formation energies of the graphene edge attached to S-I ([-110] oriented step) with  $\Delta\theta$  of 0°, 13.9°, 17.8°, 22.4° and 30°. Here, the edge of the graphene nanoribbon is used to model the graphene edge and thereafter. (b) Optimized structures and formation energies of the graphene edge attached to S-II ([001] oriented step) with  $\Delta\theta$  of 0°, 10.9°, 17.0°, 21.8°, and 30°. (c) Optimized structures and formation energies of the graphene edge attached to S-III (76.74° deviated from [-110] direction) with  $\Delta\theta$  of 0.6°, 8.5°, 13.3°, 16.7°, and 27.2°.

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