Supplementary information

Semiconducting Graphene on Silicon from First-Principle Calculations

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Models. Our supercell structure is constructed of 6 layers of Si (111) /Si (100) surfaces and the monolayer/bilayer of graphene. Meanwhile, Si (100) surface reconstruction of 2 ×1 dimer is considered. The thickness of Si layers is chosen to be 6 layers for Si (111) surface and 5 layers for Si (100) surface with the bottom layer passivated by hydrogen atoms. And the Si atoms of the bottom layer together with the passivated hydrogen atoms are fixed during DFT optimization. We also test Si surface with more layers and it will not affect the results and conclusions.

The vacuum region in the vertical direction is set to be at least 10 Å in order to ensure enough separation between periodic images. Here, we also consider the interaction between graphene and Si surfaces whose dangling bonds passivated by H atoms.

In order to make the model of the graphene / Si, it is necessary to introduce stretching, since there is lattice mismatch between graphene and Si. Then we relax the graphene / Si to obtain the stable binding structure. Similar methods have been applied to study graphene-SiO_2 interface (Phys. Rev. Lett. 2011, 106, 106801.) and graphene-Si(111) interface (Phys. Rev. Lett. 2013, 110, 176805). A 4.1 % stretched Si (111) surface is used to fit a (3 × 3) graphene supercell. A 3% and 4.1 % stretching along a-orientation and b-orientation of Si (100) surface are used to fit the graphene supercell. Because of this lattice mismatch, it requires an elastic adjustment at the interface. If this flexibility achieved exclusively *via* stretching the graphene layer, the

elastic energy would be equivalent to 0.20 eV and 0.17eV per graphene unit cell for Si (111) and Si (100) surface, respectively.

To elucidate how the energetic and electronic structure of graphene rely on the local configuration on Si (111), we considered three representative arrangements where an silicon atom is situated directly below either: a C atom, the center of a C-C bond, or the hollow site at the center of the C hexagonal ring, which are classified as the top (T), the bridge (B), and the hollow (H) configurations, respectively, as shown in Figure S1.

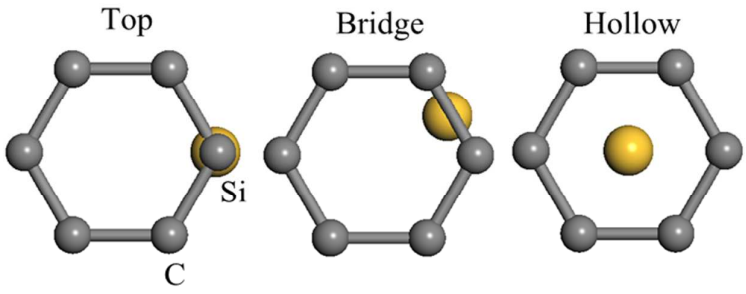

Figure S1. Three representative configurations of graphene on Si (111). Graphene are represented by gray balls (carbon atoms). We select one silicon atom from Si (111) surface and represent it by a yellow ball. We name three representative configurations as “Top”, “Bridge”, and “Hollow” and we use T, B, and H as the symbols to represent them.

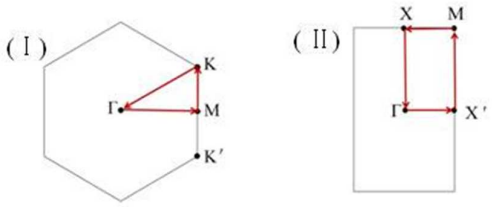

Figure S2. (Ⅰ) First Brillouin zone of graphene/Si (111) system with letters designating special points and with the lines along which the band structure is displayed. (Ⅱ) First Brillouin zone of graphene/Si (100) system with letters designating special points and with the lines along which the band structure is displayed.

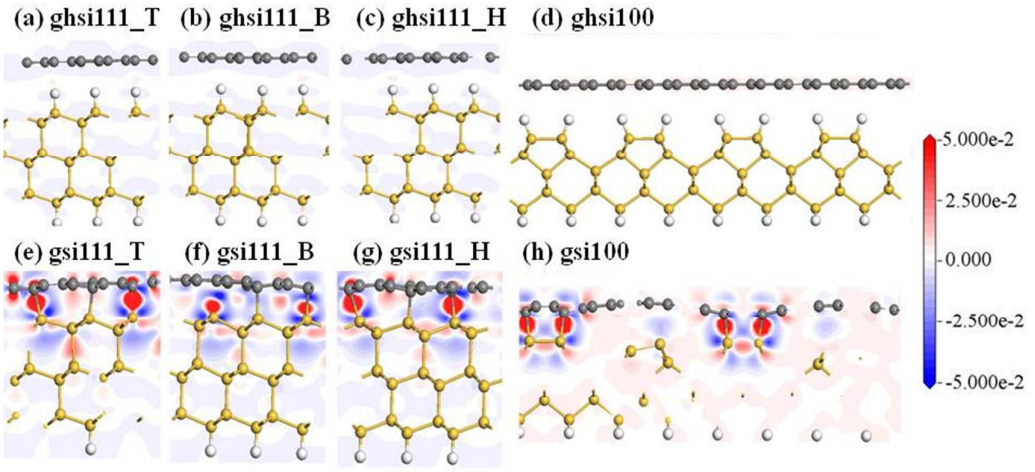

Figure S3. Different charge density of (a) ghsi111_T (b) ghsi111_B (c) ghsi111_H (d) ghsi100 (e) gsi111_T (f) gsi111_B (g) gsi111_H (h) gsi100. See Figure 1 for the definitions of ghsi111_T etc. Red and blue colors represent the increase or decrease of charge density, respectively.

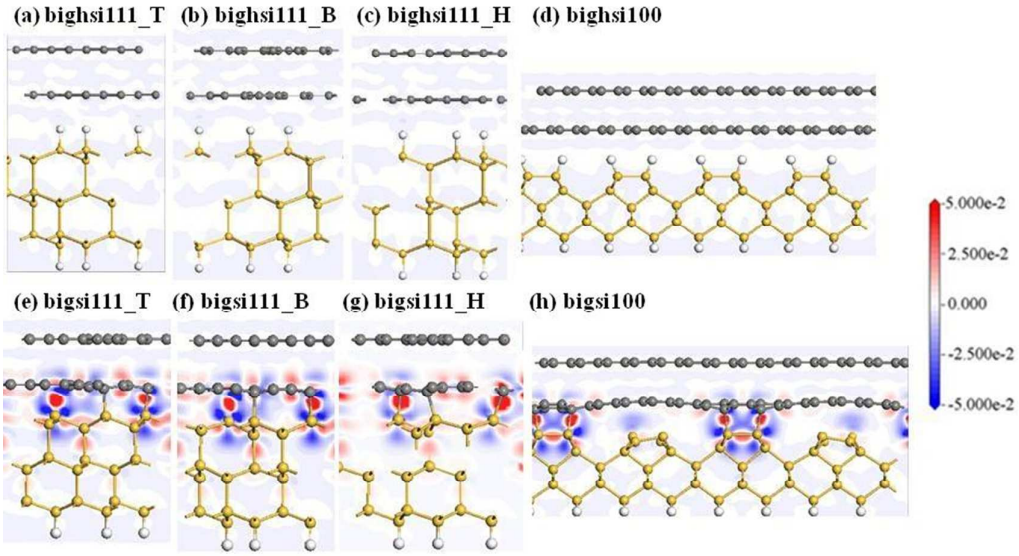

Figure S4. Different charge density of (a) bighsi111_T (b) bighsi111_B (c) bighsi111_H (d) bighsi100 (e) bigsi111_T (f) bigsi111_B (g) bigsi111_H (h) bigsi100. See Figure 1 and Figure 2 for the definitions of bighsi111_T *etc*. Red and blue color represent the increase or decrease of charge density, respectively

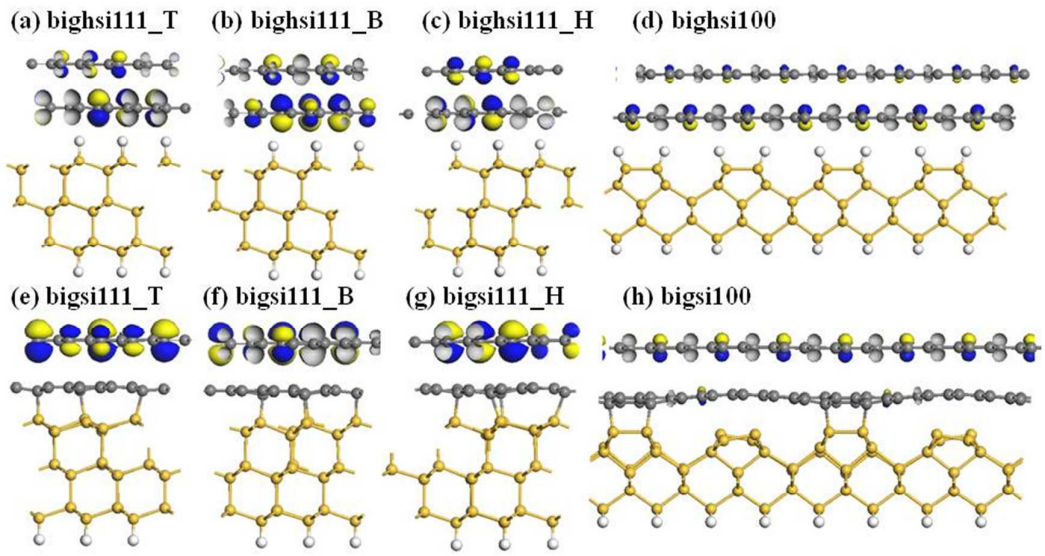

Figure S5. HOMO orbital of (a) bighsi111_T (b) bighsi111_B (c) bighsi111_H (d) bighsi100 (e) bigsi111_T (f) bigsi111_B (g) bigsi111_H (h) bi gsi100. See Figure 1 and Figure 2 for the definitions of bighsi111_T *etc*.

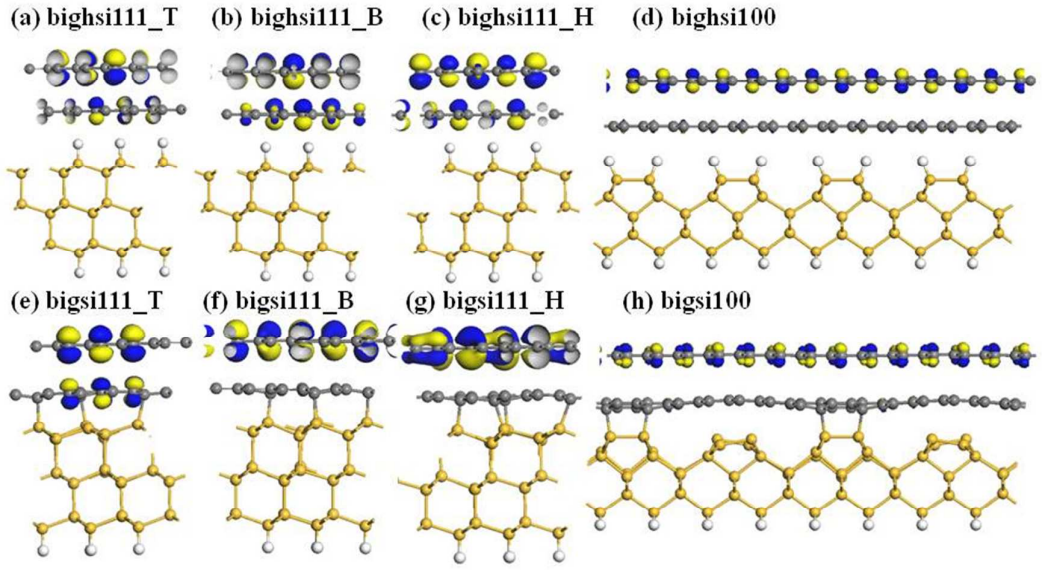

Figure S6. LUMO orbital of (a) bighsi111_T (b) bighsi111_B (c) bighsi111_H (d) bighsi100 (e) bigsi111_T (f) bigsi111_B (g) bigsi111_H (h) bigsi100. See Figure 1 and Figure 2 for the definitions of bighsi111_T *etc*.