Supporting Information for

What Are Grain Boundary Structures in Graphene?

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I. Benchmark of Global Optimization for Interface Structures by DE

To test the performance of our algorithm for searching GBs, we select a well-known symmetric GB with tilting angle 13.17° as shown in Figure S1. In this case, there are 12 carbon atoms in the optimization region $(N_{opt} = 12)$. The DE algorithm can find the ground state structure with one pentagon and one heptagon at the symmetry line rather easily: All 10 independent runs find this structure eventually and the average generation of the runs is 5.9. Performance of our algorithm is discussed in more details in the main text.



Figure S1. Symmetric GB with tilt angle 13.17° with two unit cells. Structure was found by DE. The gold atoms are those in the optimization layer with $N_{opt} = 12$ in this case. At the edges, the carbon atoms are passivated by hydrogen atoms as shown in gray.

II. Mechanical Property of Armchair-Zigzag GBs

Since a counterintuitive conclusion that graphene becomes stronger with higher density of defects in more tilted GBs was reported, [S1] the strength of graphene with the existence of GBs attracts much research attention. Further study indicates the strength of graphene also depends on the arrangements of defects. [S2] These seemingly complicated behaviors have been well explained by superposition of the stress fields from individual dislocations. [S3] These works pointed out the importance of detailed atomic stress of the critical bonds in GBs that could be decisive in the failure behavior of graphene under strain. (The finite length of the GB is also known for affecting the strength of polycrystalline graphene, see Ref. [S4]. In this work, we only consider the GBs with infinite length.) Considering that our newly found GB-II with a clean pentagon-heptagon chain has much lower formation energy than the defects-gathered GB-I, it is expected that GB-II possesses better mechanical property.



Figure S2. (a) The stress of GB-I and GB-II with strain applied perpendicular and parallel to the GBs. (b) Statistics of number of bonds of GBs. Pristine graphene has only one bond length at 1.41 Å (DFT result). Bonds in GB-I are from 1.36 Å to 1.51 Å, while bond lengths in GB-II are more close to that of pristine graphene. (c), (d) Schematic showing of bond breaking of GB-I and GB-II, respectively, with strain perpendicular to the GBs.

We expand the periodic structures to supercells about 100 nm in length and 30 nm in width. We apply the uniaxial strain along the directions either perpendicular or parallel to the orientation of GBs, and get the corresponding stress components of σ_{zz} and σ_{xx} , respectively, as shown in Figure S2(a). In both directions, GB-II outperforms GB-I on the strain at failure and the final stress, showing a better mechanical response to the external engineer strain (perpendicular to GB: 6% larger strain and 2% larger stress; parallel to GB: 5% larger strain and 9% larger stress). We show in Figure S2(b) the bond length distribution in GBs, i.e., those form the pentagons and heptagons. Clearly, bonds of GB-II are much closer to the bond length in pristine graphene, while bonds of GB-I appear more dispersive in length, indicating larger structural distortion and thus weaker mechanical strength of GB-I compared with GB-II. To understand the failure behavior of both structures from a microscopic perspective, we plot the bond breaking of GB-II and GB-II in Figure S2(c) and (d) with strain applied perpendicular to GBs, since this component of stress directly reflects the GB normal strength. [S2] We find two common features in the bond-breaking process of both GB-I and GB-II. First, bond-breaking begins in GB. In GB-I, it is the shared edge of two heptagons at the gathering of three defects

that first breaks, and in GB-II, the bond shared by one pentagon and one heptagon breaks first; Second, bonds that are (almost) parallel to the strain direction are the first to break, which is easy to understand because the increase in the bond length of such bonds is the largest.

III. Electronic Structure of Armchair-Zigzag GBs

Electronic structure is one of the major properties of graphene, with both scientific and technological importance. To help comparing the electronic structures of GB-I and GB-II, we perform first-principles calculations using the periodic structures (not supercells but unit cells) that we mentioned above.

Along the GB direction in the reciprocal space, both structures are metallic, as indicated by the band structures in Figure S3(a) and (b). Difference between GB-I and GB-II appears at the second band above the Fermi level at the Γ point: the marked band [pointed by arrow in Figure S3(a)] of GB-I is less dispersive than that [pointed by arrow in Figure S3(b)] of GB-II, indicating the marked band is more localized in GB-I. Partial charge density distribution (shown as insets in Figure S3) of the marked band at Γ point in two structures confirm that the states are localized at the GBs, and this state in GB-II is more delocalized in real space. This may due to the certain topology of the two GB structures. The states of the marked bands are mainly localized to the gathering point of the one pentagon and two heptagons in GB-I, whereas are relatively evenly distributed along the pentagon-heptagon chain in GB-II. The low effective electron mass of the GB related band in GB-II may suggest better transport properties along the GB when electrons are doped by external gate voltage.



Figure S3. (a), (b) Band structures calculated for GB-I and GB-II, respectively. The blue arrows point out the bands of the GB (defects) states, showing different properties in two structures. The insets show partial charge density distribution (in yellow) of the marked band at Γ point of two structures, indicating that of GB-II is more delocalized. (c), (d) Simulated STM images for occupied states of GB-I and GB-II, respectively. (e), (f) Simulated STM images for unoccupied states of GB-I and GB-II, respectively. The two structures are distinguishable by STM.

Experimentally, STM has been widely used to probe the structure of GBs in graphene. [S5] According to the Tersoff-Hamann approximation [S6] that the tunneling current is proportional to the local density of states of the surface, we simulate the STM images by integrating the charge density of the occupied (unoccupied) states within the range of 1.5 eV below (above) the Fermi level. [S7] Figure S3(c) – (f) are the simulated STM images for GB-I and GB-II, showing the electron states right below the Fermi level are localized to the pentagons, while those right above the Fermi level are localized to the heptagons. According to our simulations, the two structures can be distinguished by STM experiment. In GB-I, the occupied states show the separate pentagon points to the dent formed by the other three pentagons [Figure S3(c)] and the unoccupied states show explicitly two heptagons touching [Figure S3(e)]. However in GB-II, the separate pentagon points away to the dent [Figure S3(d)] and all heptagons are separate [Figure S3(f)]. Thus, STM becomes an effective technique to verify our newly found GB-II structure experimentally.



Figure S4. Structures of (a) GB-I and (b) GB-II used for calculating the magnetism at the zigzag edges. Arrows show the spin direction of the FM states at the zigzag edge. Note that there are 7 atoms at the zigzag edge, which is incompatible with the AFM spin configuration, therefore in practice, we used the supercells that double the unit cells shown above along the direction parallel to GB. Results show that the ferromagnetism is sustained in both GB-I and GB-II.

Usually for a normal zigzag carbon nanoribbon, the two edges are antiferromagnetically (AFM) coupled, but it is proved by first-principles calculations that the ferromagnetism of the zigzag edge is sustained with the other edge armchair shape, using a strained GB-I structure. [S8] To see whether the ferromagnetism of the zigzag edge is still stable in our new GB structure, we performed spin-polarized calculations. We narrow the slabs of GB-I and GB-II in consistent with the previous calculations [S8] (Figure S4). We found the ferromagnetism of the zigzag edge of two structures are both sustained. We define to represent the energy difference of FM and AFM states of the zigzag edge with the number of carbon atoms at this edge. We found $\Delta\epsilon$ (GB-I) = -0.011 eV and $\Delta\epsilon$ (GB-II) = -0.012 eV, which indicates that FM is even more enhanced in GB-II. As for the FM states, the magnetic moment averaged to each carbon atom at the zigzag edge is 0.197 $\mu_{\rm B}$ and 0.210 $\mu_{\rm B}$ for GB-I and GB-II, respectively. Taken together, GB-II structure could better stabilize the FM state of the zigzag edge comparing with GB-I, and could also increase the FM moment on the edge.

IV. All Structures Studied in This Work

Below shows all the symmetric GB structures studied in this work. Some important information, if needed, is added in the parenthesis after the degree shown in the following three structures: 2D means that at this specific GB angle, this structure has the lowest formation energy if we constrain all the atoms in the 2D plane; 3D means the similar, but we allow the fluctuations of the structures in the third dimension; by adding N, we point out that this structure has not been reported before to our best knowledge. [S9, S10, S11]



Figure S5. (1, 0) dislocation. All structures with different GB angles of this type studied in this work have been shown above. "2D" means this structure has the lowest formation energy under this angle in 2D case, and adding "3D" means this is the structure with lowest energy if we allow fluctuations in the third direction perpendicular to the 2D plane.



Figure S6. (1, 0) + (0, 1) dislocation. All structures under different angles of this type studied in this work have been shown above. By adding "2D", we mean this structure has the lowest formation energy under this angle in 2D case, and adding "3D" means this is the structure with lowest energy if we allow fluctuations in the third direction perpendicular to the 2D plane. New structures proposed in this work are indicated by adding "N".



Figure S7. Transition region. All structures under different angles of this type studied in this work have been shown above. By adding "2D":, we mean this structure has the lowest formation energy under this angle in

2D case, and adding "3D" means this is the structure with lowest energy if we allow fluctuations in the third direction perpendicular to the 2D plane. New structures proposed in this work are indicated by adding "N".



Figure S8. (1, 1) dislocation. All structures under different angles of this type studied in this work have been shown above. Adding "3D" means this is the structure with lowest energy if we allow fluctuations in the third direction perpendicular to the 2D plane. New structures proposed in this work are indicated by adding "N".

References

- [S1] R. Grantab, V. B. Shenoy and R. S. Ruoff, Science 2010, 330, 946.
- [S2] Y. Wei, J. Wu, H. Yin, X. Shi, R. Yang and M. Dresselhaus, Nature Materials 2012, 11, 759.
- [S3] B. I. Yakobson and F. Ding, ACS Nano 2011, 5, 1569.
- [S4] Z. Song, V. I. Artyukhov, B. I. Yakobson and Z. Xu, Nano Lett. 2013, 13, 1829.

[S5] Q. Yu, L. A. Jauregui, W. Wu, R. Colby, J. Tian, Z. Su, H. Cao, Z. Liu, D. Pandey, D. Wei, T. F. Chung, P. Peng, N.

P. Guisinger, E. A. Stach, J. Bao, S.-S. Pei and Y. P. Chen, Nature Materials 2011, 10, 443.

- [S6] J. Tersoff and D. R. Hamann, Phys. Rev. B 1985, 31, 805.
- [S7] D. E. P. Vanpoucke and G. Brocks, Phys. Rev. B 2008, 77, 241308(R).
- [S8] J. Zhou, T. Hu, J. Dong and Y. Kawazoe, Phys. Rev. B 2012, 86, 035434.
- [S9] O. V. Yazyev and S. G. Louie, Phys. Rev. B 2010, 81, 195420.
- [S10] Y. Liu and B. I. Yakobson, Nano Lett. 2010, 10, 2178.
- [S11] T.-H. Liu, G. Gajewski, C. W. Pao and C.-C. Chang, Carbon 2011, 49, 2306.