Supplementary Information for

Conserved Atomic Bonding Sequences and Strain Organization of Graphene Grain Boundaries

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Materials and Methods

Graphene Synthesis

Graphene is grown on a polycrystalline copper foil in a quartz tube furnace. Copper foil (Alfa Aesar, 25 μ m thick, 99.999% purity) is loaded into a 1.5 inch quartz tube and heated under a H₂ flow (5 sccm) at a pressure of 150 mTorr and temperature of 1035 °C for 1.5 hours. For graphene growth, methane is introduced into the furnace and flowed (35 sccm) for 15 minutes with a growth pressure of approximately 400 mTorr. This produces full graphene coverage over the entire copper surface. Raman spectroscopy is acquired using a Renishaw Micro Raman microscope with a 633 nm laser to check the synthesis.

Graphene TEM Sample Preparation

The graphene membranes are fabricated using a direct transfer of graphene from copper substrates to a TEM grid. A commercially available TEM grid (Quantifoil Micromachined Holey Grid R 1.2/1.3) is placed upon the graphene coated copper substrate and a drop of isopropyl alcohol (IPA) is dropped onto the TEM grid. The IPA is allowed to evaporate, allowing the supporting carbon film to come into contact with the sample surface. The resulting grid-copper stack is floated onto a freshly prepared etchant solution. The copper is etched with an ammonium persulfate etchant solution prepared by mixing the solid salt with 18.2 M Ω water (5g in 200 mL). Without submerging the sample, the stack is scooped out of the etchant solution and floated onto 18.2 M Ω water. This is repeated for a thorough rinsing of the sample. The sample is then removed from the water surface and the solution is wicked away carefully using a laboratory absorbent (Kimwipe). Lastly, the sample is placed on a hot plate in a fume hood and heated to 200 °C for 2 hours prior to insertion of the sample into the TEM column.

Aberration Corrected High Resolution Transmission Electron Microscopy (AC-HRTEM) of Graphene

All AC-HRTEM data was acquired using TEAM 0.5 at the National Center for Electron Microscopy (NCEM) in Lawrence Berkeley National Laboratory (LBNL). The microscope is a modified FEI Titan microscope with a high brightness Schottky-field emission gun, monochromator, and spherical aberration corrector. The microscope is operated at 80 kV with the monochromator turned on to provide an energy spread of approximately 0.11eV. Individual images were acquired with exposures of 0.75 to 1 second. Exit wave reconstruction of the electron wave function was performed using 20 or 40 individual images taken at indicated defocus steps of 2 or 1 nm, respectively.

Exit Wave Reconstruction of AC-HRTEM Through Focal Series Micrographs

The exit wave reconstruction from focal series was performed using a custom code written in MATLAB, using a Gerchberg-Saxton method with previously described modifications (31,32). Numerical aberration correction was performed using a gradient search method, augmented by taking into account the crystallographic symmetry in the pristine lattice regions. Both the detector modulation transfer function and the non-uniform monochromated illumination surface were modeled and corrected. Image alignment was performed iteratively using the algorithm given by (33).

Realspace Strain Measurements in Graphene Grain Boundaries

First, we determine the initial atomic positions from intensity peaks in the micrograph. These peak positions are further refined by fitting 2D Gaussian functions to each of the positions simultaneously. Best-fit lattices for each grain are computed using linear regression. At the grain boundary, each atomic position is assigned to the grain that had the closest ideal lattice position. For each atomic position, displacement vectors are defined as the deviation from the ideal lattice positions. These measurements are resampled into continuous 2D displacement maps using Gaussian kernel density estimation with a bandwidth equal to the unit cell length. The parallel strain, \boldsymbol{e}_{xx} , perpendicular strain, \boldsymbol{e}_{yy} , shear strain, \boldsymbol{e}_{xy} , and local rotation, $\boldsymbol{\theta}$, are derived from the gradient of the displacement map, which is calculated by numerical differentiation of the displacement maps.

Molecular Dynamics Uniaxial Tension Simulations

Uniaxial tension simulations are performed using the molecular dynamics (MD) software package, Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) (34,35). The atomic potential used to model graphene is the Adaptive Intermolecular Reactive Bond Order (AIREBO). The default C-C bond cutoff length was set to 1.92 Å. Periodic cells for all graphene sheets were used with typical cell dimensions of 200 by 100 Å. Geometry optimization is performed and a uniaxial tension is applied to the system with a strain rate of 1 x 10^9 s⁻¹.



Figure S1. Atomic positions at a graphene grain boundary. (a) Exit wave intensity of a graphene grain boundary with the overlaid crosses marking the measured positions of every atom in the two atomic lattices. (b) Magnified area from the boxed region of a.



Figure S2. Large area strain mapping of graphene grain boundary. (a) Parallel strain, ε_{xx} . (b) Perpendicular strain, ε_{yy} . (c) Shear strain, ε_{xy} . (d) Local lattice rotation, θ . Strain scale bars are +/- 1.0 % for (a) to (c). Scale bar for (d) is +/- 0.5 degrees. Lateral scale bar is 2 nm.



Figure S3. Periodic graphene grain boundary structures. (a) Symmetric (3,1)|(3,1) tilt grain boundary. (b) Asymmetric (7,0)|(4,4) tilt boundary.



Figure S4. Experimental GB1 versus theoretical structure. (a) Experimental GB1 structure used for MD uniaxial tension simulation. (b) Theoretical (3,1)|(3,1) structure used for MD uniaxial tension simulation.



Figure S5. Experimental GB2 versus theoretical structure. (a) Experimental GB2 structure used for MD uniaxial tension simulation. (b) Theoretical (7,0)|(4,4) structure used for MD uniaxial tension simulation.

References

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