Supporting Information: Twinning and Twisting of Tri- and Bi-layer Graphene

*Lola Brown[§1], Robert Hovden[§2], Pinshane Huang[2], Michal Wojcik[1], David A. Muller[2,3] and Jiwoong Park[1,3 *]*

[1] Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, USA

[2] School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853

[3] Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, USA.

[§] These authors contribute equally to the work.

* Correspondence e-mail: jpark@cornell.edu

Supporting Information Content

I. Methods

a. Graphene growth:

Graphene was grown on Cu foil (99.8% Alfa Aeasar, #13382) in a hot wall tube furnace, which was heated while flowing H_2 (ultra high purity grade; Air Gas, Inc.) at a pressure of ~2 Torr. All growths were conducted inside a Cu enclosure. Growths parameters (temperature, flow rates, times) were changed as follows: Figure 1a - 930 C^o, 120 sccm H_2 flow, 1 sccm CH_4 flow, 90 min; Figure 1b,c and 5 - 950 C^o, 120 sccm H_2 flow, 1 sccm CH_4 flow, 90 min; Figure 2,3,4 – 980 C^o, 60 sccm H_2 flow, 1 sccm CH_4 flow, 90 min (Kevek innovations, hot wall 1" tube furnace).

b. SEM characterization:

The graphene was imaged directly on the Cu growth substrate, by the backscatter detector of a scanning electron microscope (SEM) (Zeiss Ultra) operated at 1kV.

c. TEM characterization:

The graphene was transferred to a TEM grids by the following procedure: a protective poly(methylmethacrylate) (PMMA, 2% 495K in Anisol) was spin-coated on the Cu/Graphene substrate. The substrate was then floated on a dilute aqueous iron(III) chloride solution (Transene, Cu etchant CE-200) in order to etch the Cu from the backside. The remaining PMMA/graphene membrane was then washed with copious amounts of water, and transferred on the 5 and 10 nm thick silicon nitride TEM support grid (TEM Windows, #SN100-A05Q33A and #SN100-A10Q33). The grids were gently annealed (350 C^o, 3 hours) in air to remove the PMMA[1].

Dark-field TEM was conducted on an FEI Technai T12, operated at 80 kV, as to avoid damage to the graphene lattice[1]. In order to collect electrons diffracted from a specific crystallographic orientation, an aperture was placed on the back focal plane of the diffraction pattern from the area of interest (down to 300 nm radius). For most DF-TEM images we used the smallest aperture available (0.09 $Å^{-1}$). For Figure 2e we used a larger aperture (0.26 $Å^{-1}$) to collect the diffracted intensity from two crystallographic orientations. With the aperture in place, we take a real space image, which highlights the graphene crystals corresponding to the chosen crystallographic orientation. For multi-crystalline regions, this process is repeated for each diffraction spots within a 60^o arc. Images from each aperture position are colored and overlaid to create a complete color-coded image.

d. Diffraction Spot Analysis

Diffraction spot intensities were determined by first fitting a five parameter two-dimensional Gaussian and a constant background level to a windowed region of the each diffraction spot. As discussed by Meyer *et al.*[2], the width of the Gaussian changes from surface variation in the graphene layers. Therefore, it is important to calculate the intensity from the area under the Gaussian fit. Supp. Fig. 5-*left* shows a diffraction spot series for a single diffraction spot, over a range of tilts. Supp. Fig. 5-*right* shows the Gaussian fits to the data.

1. Huang, P. Y.; Ruiz-Vargas, C. S.; van der Zande, A. M.; Whitney, W. S.; Levendorf, M. P.; Kevek, J. W.; Garg, S.; Alden, J. S.; Hustedt, C. J.; Zhu, Y.; Park, J.; McEuen, P. L.; Muller, D. A. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature* **2011**, *469*, 389

2. Meyer, J.C.; Geim, A. K.; Katsnelsond, M. I.; Novoselovc, K.S.; Obergfelle, D.; Rothe, S.; Girita, C.; Zettl, A.; On the roughness of single- and bi-layer graphene membranes. *Solid State Communications* **2007** 143, 101

II. Figures

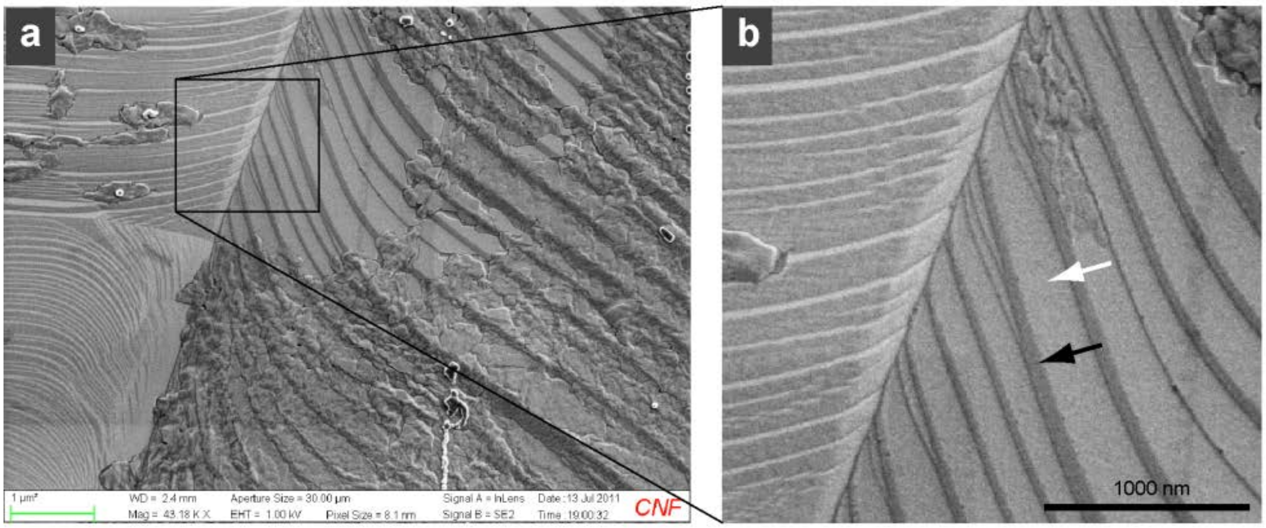

Figure S1: **Copper steps on graphene-coated Cu**. a) SEM image of the copper steps on graphene-coated Cu foil. b) zoom in of an area in (a). The average ledge width on the Cu grain to the right is 170 nm (white arrow), while the step size is 50 nm (black arrow). The step sizes depend on the Cu grains morphology, as can be seen from the different morphology on the left of (a).

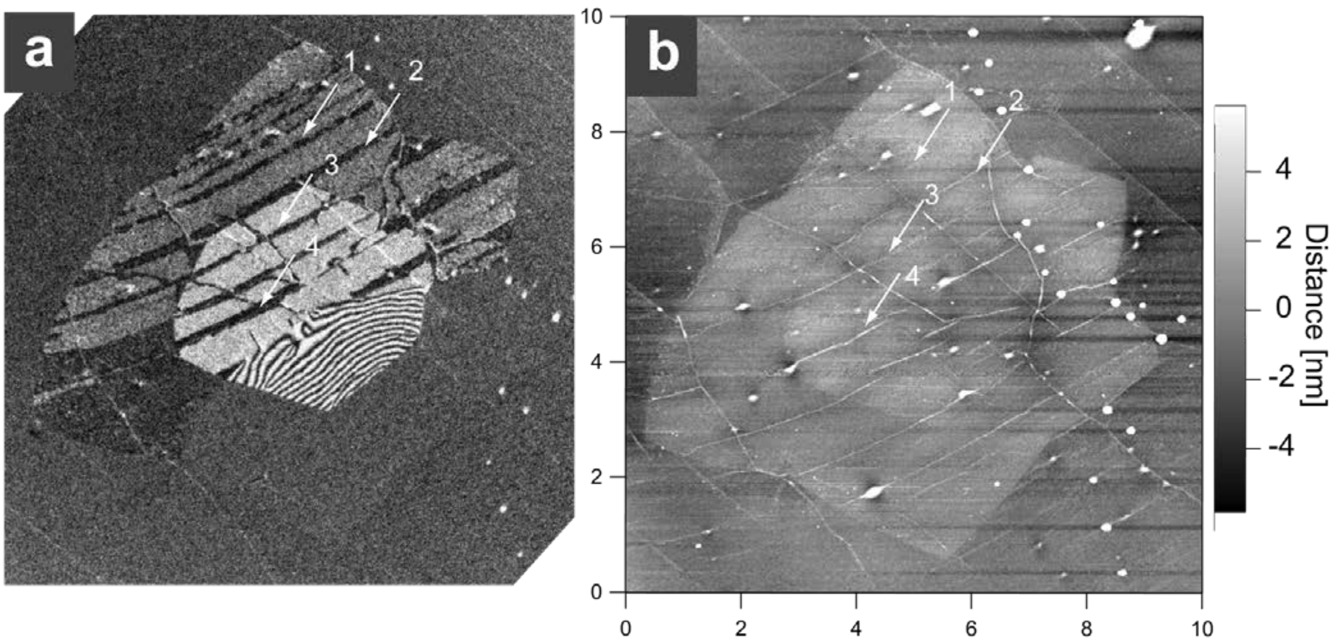

Figure S2: **Height steps in AFM image correspond to twinning sites in DF-TEM image**. a) DF-TEM image of the same area as Figure 3, taken with an aperture around peak $\emptyset_1$. b) AFM height image of the same area. White arrows point to thin long folds which correspond to twinning sites in the TEM image.

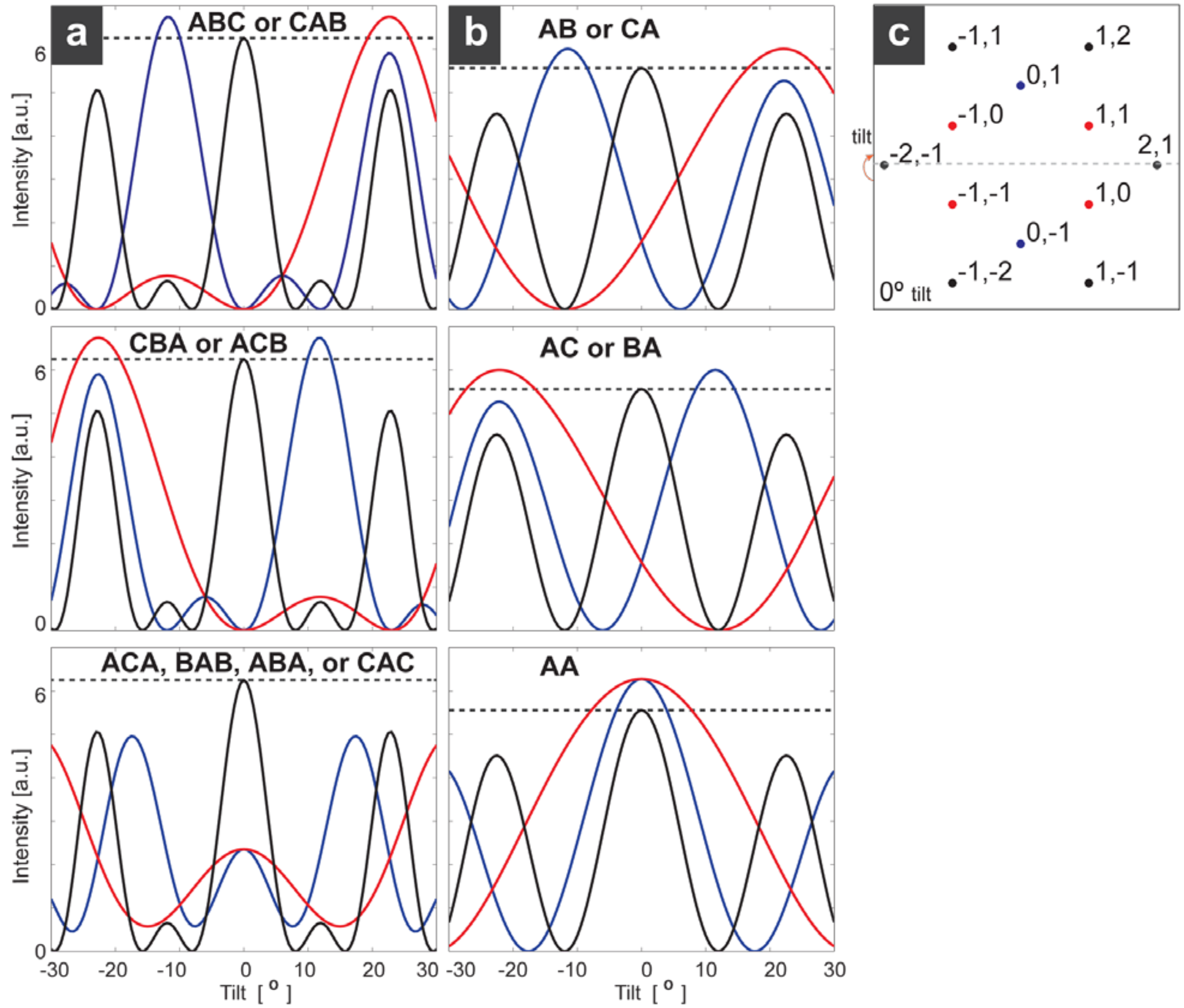

Figure S3: Diffraction tilt patterns for oriented TLG and BLG. a) Diffraction tilt patterns of trilayer Bernal and rhombohedral stacked graphene, assuming a flat Ewald sphere. b) Diffraction tilt patterns of bilayer Bernal stacked graphene, assuming a flat Ewald sphere. c) color-coded diffraction peak pattern and tilt axis.

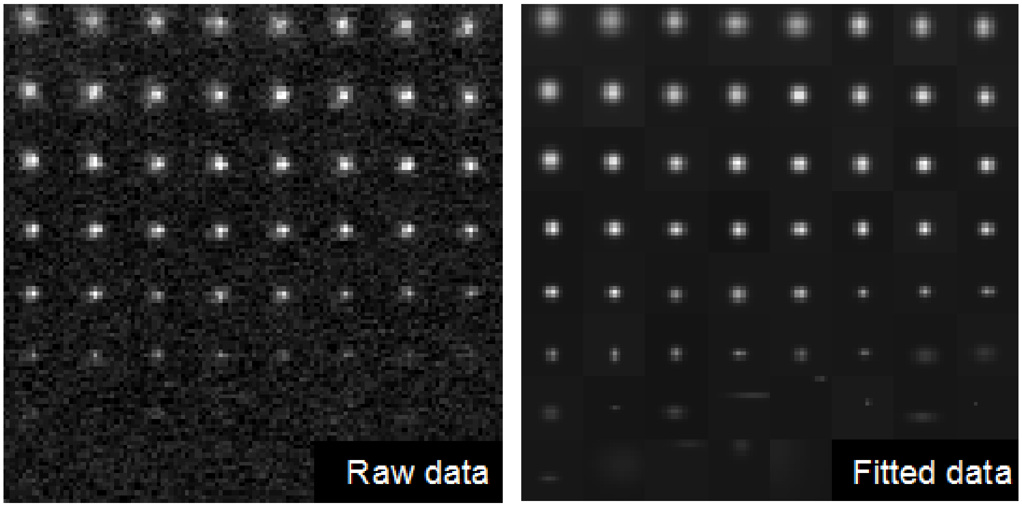

Figure S4: Diffraction peak analysis. Stitched mosaic of tilt-series (±15°) data of the (-1,1) diffraction spot (left) and the corresponding Gaussian fit (right). Figure reads top-left (lowest angle) to bottom right (highest angle). When the intensity is low, as seen for the higher tilts (bottom region), the Gaussian fits are no longer physical, instead characterizing local noise.

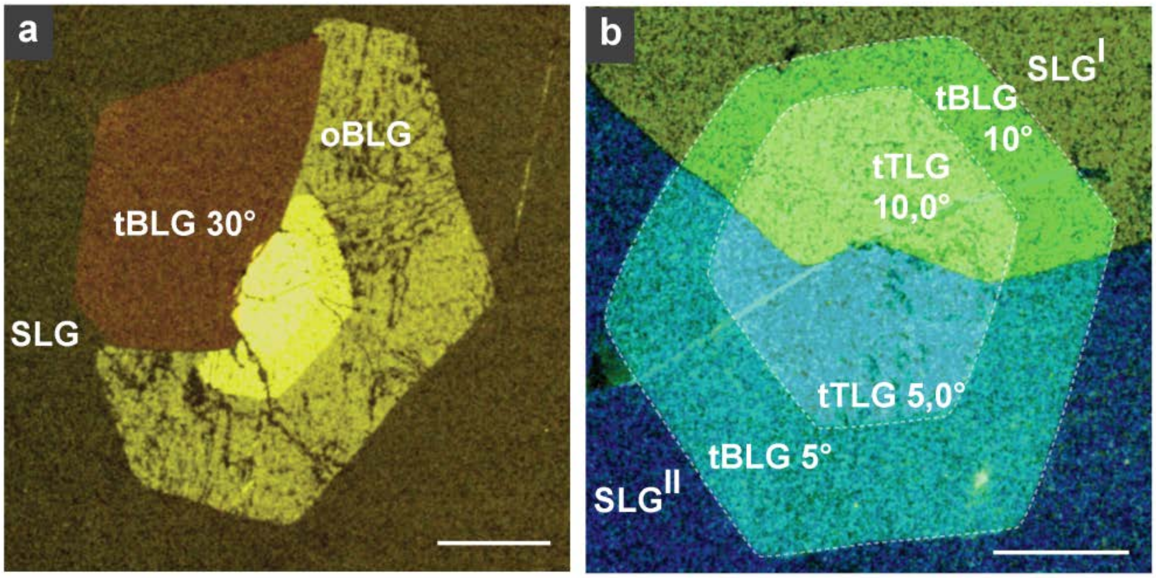

Figure S5: Examples of twist and area analysis of continuous tBLG and oBLG regions. a) False-color DF-TEM shows a multilayer patch with two connected bilayer regions; a twisted region (30 ^{o}) and a BS region. Scale bar is 1 micron. b) false-color DF-TEM shows a second and third layers (borders defined by a dotted line), lying on top of two single layers with different crystalline orientation (SLG^{I} and SLG^{II}). Scale bar is 1 micron.