

**Supp. Figure 1| Characteristics of growth and copper grain size a,** Representative Raman spectrum of single-layer graphene samples on copper. The shape and size of the G and 2D peaks show that the graphene is predominantly single layer. In most samples, we measure a very small or, as in this spectrum, undetectable D peak, indicating that we are growing graphene with little disorder. The sloping background in the spectrum is from the copper growth substrate, as this spectrum is taken before transfer to the TEM grid. **b**, SEM image of the copper substrate after graphene growth. Because of electron channeling effects, different grains appear with different brightness. This area is near the edge of the copper foil, showing that the copper grain size ranges from tens of microns near edges of the foil to millimeters in the bulk of the foil.



Supp. Figure 2 | Raw and low-pass filtered images of the graphene lattice (a) and grain boundaries (b,c) . a-c, Raw ADF-STEM images with Fourier transforms (inset) and masks (insets, color) used to produce the filtered images in d-f. The Fourier region inside the masks are applied with a smoothing region of 5-10 pixels and then inverse transformed to form the images in (d-f).



# Supp. Figure 3| Electron-beam induced bond rotations. a-c,

Sequential Fourier-filtered images of identical regions of a grain boundary. Heptagons (red), pentagons (blue), and hexagons (green) which change between images are highlighted. **d-f**, images without overlays. While the grain boundary does not undergo major structural rearrangement, very high-dose imaging appears to induce bond rotations. From a to b, a pentagon-heptagon pair rearranges to form two hexagons. From b to c, a pentagonheptagon pair rearranges to form two hexagons, and a hexagonpentagon pair switch positions. These changes induce slight accommodations by nearby atoms/bonds. The brighter regions on the right hand side of the image represents growing surface contamination. Scale bars 5 Å.



Supp. Figure 4| Lines of surface contamination often mark grain boundaries. a, Low-magnification ADF-STEM image of a region with three lines of contamination (lines meeting at center) and a wrinkle in the graphene (thick band, lower left) b, Fast Fourier transform (FFT) of a bright-field STEM image of the region in the area marked in (a). c, BF-STEM image formed from taking the inverse FFT of (b) using the colored masks marked. This image shows that the lines of contamination, which are ~5-10 nm wide, occur along grain boundaries.





**Supp. Figure 5** | **DF processing and analysis. a**, Set of raw DF-TEM images for 6 different objective aperture locations, used to create the final composite colored grain image in (d). **b**, Diffraction pattern from a 1  $\mu$ m diameter region in the grid showing the locations of the apertures, color-coded to match (a) and (d) c, bright-field TEM image of the same area, showing no grain contrast. **d**, Final composite image marked with measurements of the grain boundary angles. Most grain boundaries are <10° or >20°. Error is ± 2-5°.



Supp. Figure 6 Additional data on global and relative grain orientations. a, Averaged SAED patterns from two samples taken in the same manner as Figure 3c. The left diffraction pattern is from Figure 3c (left). The right pattern is from an additional sample. b, Polar plots of the 2.1 Å reflection for the two diffraction patterns in (a). Plots are generated by averaging the diffraction peaks every 60 degree period. c, Statistics on relative rotations between grains taken using aberration-corrected ADF-STEM . These statistics are directly comparable to those in Figure 3b.



boundary location

Supp. Figure 7 | Large grained, aligned growths. When grains become micron-scale or larger and crystallographically aligned along only a few directions, extreme care is necessary to accurately determine grain size. a, Composite DF-TEM image from Growth Method C. b, Composite DF-TEM image from a, with the Quantifoil background subtracted so that the image only shows the graphene grains. While this image appears to show very large grains more than 30 microns across, closer examinations (c-d) reveal that these large regions are comprised of several grains separated by very small-angle grain boundaries. **c**, An enlarged image of the region outlined in b. **d**, A higher-magnification DF-image of the region outlined in c, with careful DF-imaging done to separate as many grains as possible. This detailed imaging separated two additional grains with a 2° relative rotation. The circle indicates the selected area used to form the diffraction pattern in e, which shows an additional grain boundary of less than 0.5°. This estimated grain boundary location is indicated by a dotted line in d.



# Supp. Figure 8| Moiré Fringes and identifying multi-layer

**graphene with DF-TEM.** We also identify and measure relative orientations of graphene overlapping in folds and multi-layer graphene. **a**, A moiré fringe in a graphene fold. **b**, A region with sections of 1, 2, 3, and 4 layers of graphene. Because these layers have closely-aligned crystallographic orientations, they produce moiré fringes in the DF images. When multiple layers of graphene have very disparate crystallographic orientations, they appear in separate DF-images, rather than as moiré fringe patterns.



Supp. Figure 9 | Direct comparisons between TEM ,STEM, SEM, and AFM images of grain boundaries. a, Composite DF-TEM and b, SEM images of the same region. We also show similar comparisons between c, ADF STEM, and d, AFM phase images of a second region. Decorated grain boundaries are visible in SEM, STEM, and AFM phase images. Scale bars are 250 nm.



Supp. Figure 10 | AFM indentation curves and topography. AFM topography images **a**, before and **b**, after the indentation measurement resulting in the tearing of graphene sheet along the grain boundaries of a single domain. **c**, Force plot exerted by the AFM tip as a function of the z position of the AFM piezo. At a relatively low force of about 30 nN, the force drops back down due to the graphene sheet breaking. Before this, smaller drops in the force likely corresponding to smaller tears can be observed. **d**, Corrected force plot, taking into account the tip's deflection, corresponding to the actual graphene's vertical deflection under the AFM tip. Scale bars are 200 nm.



**Supp. Figure 11 | Mobility Measurements. a,** Contrast enhanced optical image of top-gated electrically contacted graphene in four probe geometry (Scale bar 10  $\mu$ m). **b,** Side schematic of top-gated graphene device. Material thicknesses are not to scale. **c,** Four point transport measurement of graphene grown in Growth B as a function of top gate voltage. We extract a mobility of 9000 cm<sup>2</sup>/V·s from the point of largest slope (red dot).



**Supp. Figure 12 | AC-EFM data and processing. a,** Side and top schematics of suspended electrically contacted graphene. **b**, Schematic of AC-EFM measurement setup. **c**, AFM topography and **d**, phase images of a suspended electrically contacted sheet of graphene. **e**, AC-EFM images when driving the left, right and both electrodes respectively. **f**, Ratio of left and right driven electrode EFM images to both electrode driven image. This ratio is proportional to electrostatic potential along the sheet. Features due to changing contaminants and topography of the images disappear. Color bar rescaled to exclude external resistance. **g**, Single line trace from ratio image taken along blue arrow in figure (f). All images are 4.2 μm across, and dashed lines indicate electrode locations.

## **Supplementary Methods**

### **Outline:**

- 1. Raman Spectroscopy
- 2. ADF-STEM image processing
- 3. Low magnification STEM imaging of grain boundaries
- 4. **DF-TEM image overlay procedure**
- 5. **DF-TEM statistics acquisition**
- 6. More statistics on grain angles
- 7. Larger grains, multi-layer graphene, and imaging artifacts in DF-TEM
- 8. Grain imaging comparisons: DF-TEM, STEM, AFM, SEM
- 9. **AFM indentation**
- 10. Transport Mobility Measurements
- **11. AC-EFM**

### 1. Raman spectroscopy

Figure S1 shows a representative Raman spectrum of the graphene after growth on copper<sup>1,34</sup>. The shape and relative size of the G and 2D peaks show that the graphene is predominantly single layer. In most samples, we measure only a very small D peak, if it is at all discernable, indicating that we are growing graphene with very little disorder.

### 2. ADF-STEM image processing

Figure S2a-c show the raw STEM images used to produce the images in Figure 1. These images were low-pass filtered to reduce noise using masks similar to the inset in Figure S2a. To create images d and f, the masks were positioned slightly outside the 1.23 Å spot. For Figure S2e, the mask is positioned between the 1.23 and 2.13Å spots—such a tight low-pass filter was employed to make viewing the image and identifying the polygons in the lattice easier. Figure S2d-f are the final images. Figure S2d, in addition to the processing described above, was created by cross-correlating and summing ten lattice images taken in succession on the same region of the graphene lattice to improve signal-to-noise. Finally, Figure S2c,f show that we are able to get atomic resolution images of the grain boundaries. We found that bond rotations can occur at very high magnification, as shown in Figure S3, while the grain boundary does not undergo a major rearrangement.

### 3. Low Magnification STEM imaging of grain boundaries

Figure S4a shows a low magnification STEM image of three grain boundaries intersecting at a point. In this image, grain boundaries appear as bright lines due to adsorbed contamination decorating the grain boundaries. The contamination lines are roughly 4-15 nm wide in STEM. In addition, there is a much wider ( $\sim$  30 nm) line along the bottom-left of the image representing a fold in the suspended graphene sheet. Figure S4c is a color overlay of the inverse Fourier Transforms of the diffraction spots highlighted in Figure S4b, showing that the different grains meet along the lines of adsorbed contamination. We identified the contamination material decorating the grain boundaries using core-loss electron energy loss spectroscopy, which revealed that the contamination contains iron, oxygen, and carbon. The iron contamination is likely deposited during the ferric chloride etch used to remove the graphene from the copper substrate.

# 4. DF-TEM image overlay procedure

Figure S5a shows the raw DF-TEM data used to create the composite color DF-image shown in Figure 2g. We use GIMP 2 to do the overlay image processing (though any image processing software will do). First, each raw DF-image is read in as a layer and aligned by hand to the other layers if necessary. Next, the images are adjusted to maximize brightness and contrast, making sure to adjust each image to the same brightness/contrast levels. Each layer is then colorized according to the color code on the boxes, and the layers are merged. The levels in the final image are adjusted, clipping the highest and lowest intensities to enhance the image contrast. The overall color balance may be adjusted to enhance the color contrast in the image, giving the final image shown in Figure 2g. A similar process is used for all composite DF-images in Figure 2.

# 5. DF-TEM statistics acquisition

In order to extract the statistics shown in Figure 3, grain sizes and orientations were measured on three different samples.

To measure grain sizes, we determined the size of grains using raw DF-TEM images such as those shown in Figure S5a. The original image contrast was too low to be extracted by simple thresholding, but high enough that grains were clearly recognizable. To make size determination easier, we first traced the edge of each grain by hand using the Magnetic Lasso tool in Photoshop and then filled them with color. The images were then fed into ImageJ where the grains were picked out by thresholding and their areas were measured. With these methods, we counted 535 grains for a sample obtained with Growth Method A, shown in the histogram in Figure 3a. The mean grain sizes reported in the text are number-averaged grain sizes (each grain is weighted equally in the average). The area-averaged grain sizes (each grain is weighted proportionally to its area), are roughly a factor of two larger than the number-averaged sizes: Growth Method A, 520 nm; Growth Method B, 830 nm; Growth Method C:  $3.5 \,\mu$ m.

To get relative grain orientations, we referred to DF-TEM composite images and their corresponding diffraction patterns. An example is shown in S5d, where the measured angles are displayed over the grain boundaries in question. For Growth Method A, we recorded 238 data points on 8 different membranes. Error in this measurement varies by data point and is typically  $\pm 2^{\circ}$ , though it may be up to  $\pm 5^{\circ}$ , depending on whether it is clear which diffraction peak results each grain. The upper bound on the angle is determined by the size of the objective aperture, and applies to highly polycrystalline regions with very closely spaced diffraction peaks.

### 6. More statistics on grain angles

For each image in Figure 3c, we averaged diffraction patterns sampled from 50 different membranes taken from a 1200  $\mu$ m<sup>2</sup> region on a TEM grid. Each diffraction pattern is taken using a ~1 $\mu$ m diameter selected area aperture to exclude the SiN grid support. In Figure S6a, we reproduce Figure 3c(left) in the red box and also show data from an additional sample (blue box) In Figure S6b, we show the diffraction data as a polar intensity plot at 2.1 Å, with the trace color corresponding to the box color on the diffraction data in Figure S6a. In each diffraction pattern, there are small sub-peaks with ~ 5°-7° spacings, which are not as easily visible in the diffraction images.

Figure S6c shows a histogram of relative grain angle measured using STEM on 42 grain boundaries. This histogram shows the same peaks at low and high grain angles found in the grain angle histogram measured using DF-TEM.

### 7. Larger grains, multi-layer graphene, and imaging artifacts in DF-TEM

Figure S7 shows DF-TEM images of Growth C on a Quantifoil TEM grid. The Quantifoil is amorphous and thin enough (~10-20 nm) to enable DF-TEM grain imaging through the carbon support.

Close examination of the image shown in Figure S7b, which appears to show grains tens of microns in size, reveals that small-angle grain boundaries can still be present, as shown in Figure S7c-e. These results highlight the need for careful, detailed DF-TEM imaging in determining grain size in CVD graphene, especially in the presence of small angle  $< 2^{\circ}$  grain boundaries.

Identification of multi-layer graphene is also possible with DF-TEM. Figure S8 shows the moiré fringes in regions with 2-4 graphene layers resulting from closely aligned crystallographic orientations. In contrast, when different graphene layers have disparate orientations, they appear in separate layers and are readily identifiable with DF-TEM composite imaging.

# 8. Grain imaging comparisons: DF-TEM, STEM, AFM, SEM

Figure S9 demonstrates that decoration allows us to see the grain boundaries using a variety of microscopy techniques in addition to DF-TEM and ADF-STEM. Figures S9a-b show the same region of suspended graphene measured using DF-TEM and SEM. These images show a strong correlation between grain boundaries and contamination lines seen in SEM. Similarly, Figure S9c-d show the same region of suspended graphene measured using STEM and AFM phase imaging. The decoration makes the grain boundaries visible because it has increased electron-sample interaction in SEM and STEM, and because it changes the tip-surface interaction in AFM. For these imaging techniques, the graphene needs to be suspended and relatively clean. Unfortunately, we find that doing photolithography on the graphene often deposits enough carbon and other surface particles to obscure the grain boundaries.

### 9. AFM indentation

To measure the mechanical properties of graphene by AFM indentation measurements, a procedure like the one described by Lee et al. (for exfoliated graphene) was employed<sup>26</sup>. We can use the model described in that study to measure the 2D elastic modulus, obtained by fitting deflection curves to the following equation:

(1) 
$$F = \sigma \pi d + E \frac{(qd)^3}{a^2}$$

Where  $\sigma$  is the 2D pretension and *E* is the 2D elastic modulus, *a* is the radius of the graphene sheet, *d* is the deflection of the graphene at its center, and *q*, a function of the Poisson's ratio, is taken to be 1.02. We found smaller values for the effective elastic modulus, a factor of ~6 smaller than those reported by Lee et al. <sup>26</sup>, but further discussion on the possible causes of this diminished elastic response lies outside the scope of this paper, and is still work in progress.

The force is calculated by the simple equation  $F = kd_{tip}$  where k is the spring constant of the cantilever and  $d_{tip}$  is the tip deflection. Graphene's deflection is calculated by subtracting the tip deflection from the Z position of the AFM piezo (Z sensor). Plots of the Z sensor and deflection are shown in Figure S10c-d.

The breaking load was read from the force curves as the point where the force exerted on the tip returns to zero or nearly zero. Smaller breaking events, where the force experienced only small drops, could be observed in some force plots, suggesting that smaller tears in graphene can occur before its complete failure.

As mentioned in the main text, we found that failure occurs at loads of ~100 nN on average. This is for graphene membranes 3.5  $\mu$ m in diameter. In their study on exfoliated graphene, Lee *et al.* report a mean breaking force of ~1.7  $\mu$ N, independent of membrane diameter (for diameters of 1.0 and 1.5  $\mu$ m)<sup>26</sup>.

### **10. Transport Mobility Measurements**

Figure S11a-b shows an optical image and a schematic cross-section of the electrically contacted CVD graphene devices used for transport measurements, and described in the methods. We perform four probe transport measurements by applying a 30 mV source-drain bias on the outer electrodes labeled on Figure S11 a,b. We then measure both the current flowing through the drain and the voltage difference between the inner electrodes *V1* and *V2*. By dividing these two numbers and scaling by the graphene size, we get the intrinsic resistivity of the graphene  $R_{square}$ . Figure S11c shows the graphene resistivity versus top-gate voltage  $V_{TG}$ . The Dirac spectrum is clearly visible. We calculate mobility by measuring the point of maximum slope on the trace (shown by the red dot), and applying the equation:

(2) 
$$\mu = \left(\frac{\frac{10^4 \ cm^2/m^2}{C_{TG}}}{\frac{C_{TG}}{A}R_{square}^2}\right) \frac{dR_{square}}{dV_{TG}}$$

where  $C_{TG}/A$  is the capacitance per unit area of the top-gate to the graphene. The trace in Figure S11c has a mobility of 9000 cm<sup>2</sup>/V·s.

### 11. AC-EFM

Figures S12c-d show the topography and phase images of an electrically contacted suspended graphene device, which correspond directly to the device schematic shown in Figure S12a. Unlike previously shown phase images, no grains are visible on the graphene surface because these features are obscured by extra contamination accumulated during the lithographic shaping. We performed AC-EFM measurements<sup>28</sup> on electrically contacted suspended graphene membranes using the circuit shown in S12b. Figure S12e shows the measured signal when driving the left electrode, the right electrode, and both electrodes respectively. By taking the ratio of the signals when the device is driven on one side and on both sides, we cancel out signals due to contamination and changing materials and measure the relative electrostatic potential along the device. Figure S12f shows the ratios of the data in Figure S12e with the images X-Y correlated to account for spatial drift, and rescaled to exclude external resistance. Figure S12g shows the relative potential from a single line scan from one electrode to another taken along the arrow shown in Figure S12f.

34 Ferrari, A. C. et al. Raman spectrum of graphene and graphene layers. Phys. Rev. Lett. 97 (2006).