Grains and Grain Boundaries in Single-Layer CVD Graphene: An Atomic Patchwork Quilt

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Single-layer graphene can be produced by chemical vapor deposition (CVD) on copper substrates on up to meter scales(*1, 2*), making their polycrystallinity(*3, 4*) almost unavoidable. Understanding the grain structure of CVD graphene is critical because graphene grain boundaries have been predicted to significantly alter the electronic(*5-8*), magnetic(*9*), chemical(*10*), and mechanical(*11-13*) properties of graphene monolayers. By combining aberration-corrected scanning transmission electron microscopy (ADF-STEM) and dark-field transmission electron microscopy (DF-TEM), we image graphene grains and grain boundaries across six orders of magnitude in CVD graphene grown on copper. Combining these images with scanned probe and transport measurements, we probe the electrical and mechanical properties of the grain boundaries. These results, reported in Reference (4), will enable studies on the structure, properties, and control of graphene grains and grain boundaries.

To characterize graphene membranes at all length scales, we first approached the atomic-scale using ADF-STEM imaging at 60 kV. The resulting atomic-resolution images of graphene grain boundaries reveal that different grains stitch together predominantly via pentagon-heptagon pairs (Figure 1b). We next used diffraction-filtered imaging to map the shape and orientation of several hundred grains and boundaries on the scale of tens of nanometers to tens of microns. These images reveal an intricate patchwork of grains connected by tilt boundaries, with average grain sizes ranging from 250 nm up to 2-4 microns (Figure1a). We used these DF-TEM methods to directly correlate grain size with growth condition and demonstrate that the graphene grain size can be increased by over an order of magnitude with only slight changes to the growth conditions.

By correlating grain imaging with scanned probe and transport measurements, we show that grain boundaries dramatically weaken the mechanical strength of graphene membranes, but do not as dramatically alter their electrical properties. We first examined the failure strength of the polycrystalline CVD graphene membranes using atomic force microscopy (AFM). We used AFM phase imaging to locate grains and then pressed downward with the AFM tip to test the mechanical strength of the membranes. We next probed the electrical properties of polycrystalline graphene by fabricating electrically-contacted devices using graphene from graphene grown with three different growth methods on copper. By comparing these measurements against corresponding DF-TEM images from each growth, we find that surprisingly, while mobility is clearly affected by growth conditions, high mobility does not directly correlate with large grain size. These methods will be crucial both for exploring synthesis strategies to optimize grain properties and for further studies on the microscopic and macroscopic impact of grain structure on graphene membranes.

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Figures

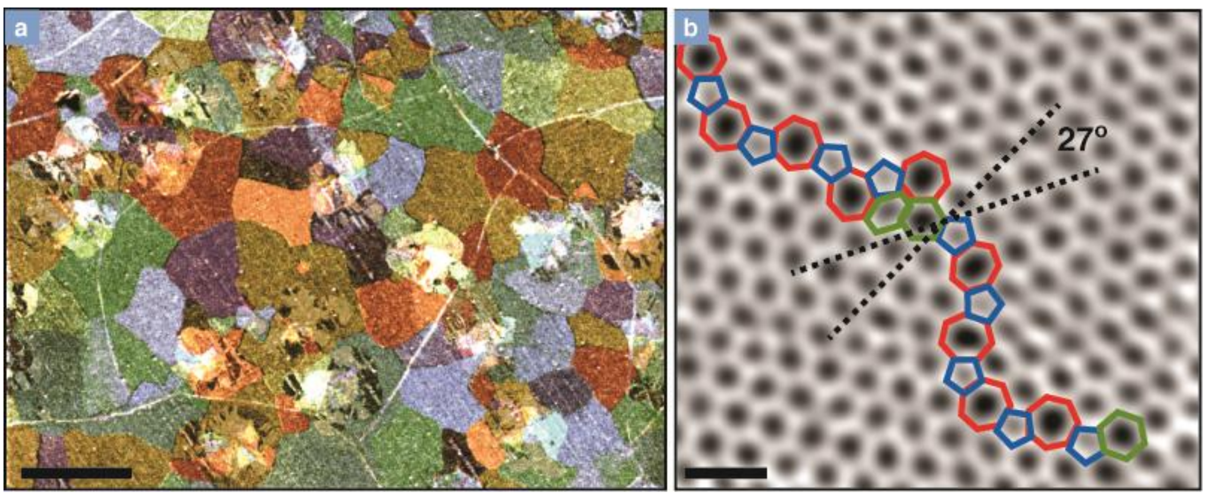

Figure 1: Images of the grain structure of CVD graphene grown on copper. (a), Composite, colored DF-TEM image of graphene grains. Each color represents graphene of a small (~5 degrees) range of in-plane crystallographic orientations. Scale bar 2 microns. (b) ADF-STEM image of the atomic structure of a grain boundary in which the two grains meet with a relative crystallographic rotation of 27 degrees. Pentagons (blue), heptagons (red), and disordered hexagons (green) make up the meandering, aperiodic structure at the grain boundary. Reproduced from Reference 4, scale bar 5 angstroms