Grain Boundary Mapping in Polycrystalline Graphene

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Graphene, with its unusual electrical, mechanical, and thermal properties, presents new opportunities in fundamental research and practical applications.1–4 Most experimental investigations of graphene have been focused on exfoliated small-area specimens, usually restricted to single-grain regions. Recently, large-area synthesis of high-quality but polycrystalline graphene has been advanced as a scalable route to applications including electronic devices.5–9 The presence of grain boundaries (GBs) may have detrimental effects on some electronic, thermal, and mechanical properties of graphene, including reduced electronic mobility,6–9 lower thermal conductivity,10 and reduced ultimate mechanical strength.11 Yet on the other hand, GBs might be beneficially exploited via controlled GB engineering.12 The study of graphene grains and their boundary is therefore critical for a complete understanding of this interesting material and for enabling diverse applications.

Since graphene is a two-dimensional one-atom-thick carbon membrane, the GB in graphene is a one-dimensional entity. This is in contrast to regular three-dimensional materials for which the GB is a two-dimensional surface. The GB of graphite has been investigated using scanning tunneling microscopy (STM) for over 20 years,13–16 and more recently, STM and other surface studies of grains and boundaries have been performed on epitaxially grown graphene on single-crystal substrates.17–22 Unfortunately, such surface probe techniques are either extremely time-consuming and not appropriate for large-area characterization13–18,20–22 or lack suitable spatial resolution in the case of low-energy electron diffraction and microscopy.18,19 Moreover, true atomic-resolution imaging at the GB of graphene unperturbed by the substrate structure has not been achieved, hindering fundamental understanding of the electronic and mechanical properties of polycrystalline graphene structures.

TEM, a direct and relatively fast imaging tool ideally suited for suspended atomically thin membranes, has been successfully applied to study adsorbates on graphene using modest-resolution machines23 and, using aberration-corrected instrumentation, to the local atomic structure of graphene itself.24–26 We show here that scanning electron diffraction in STEM mode (SED-STEM) makes possible fast and direct identification of GBs. We also demonstrate that dark-field (DF) TEM imaging techniques allow facile GB imaging for high-angle tilt GBs in graphene. GB mapping is systematically carried out on large-area graphene samples via these complementary techniques. The study of the detailed atomic structure at a GB in suspended graphene uses aberration-corrected ultra-high-resolution TEM, which shows the theoretically predicted alternating pentagon–heptagon structure along high-angle GBs.

ABSTRACT We report direct mapping of the grains and grain boundaries (GBs) of large-area monolayer polycrystalline graphene sheets, at large (several micrometer) and single-atom length scales. Global grain and GB mapping is performed using electron diffraction in scanning transmission electron microscopy (STEM) or using dark-field imaging in conventional TEM. Additionally, we employ aberration-corrected TEM to extract direct images of the local atomic arrangements of graphene GBs, which reveal the alternating pentagon–heptagon structure along high-angle GBs. Our findings provide a readily adaptable tool for graphene GB studies.

KEYWORDS: graphene · polycrystalline · grain · grain boundary · transmission electron microscopy (TEM)
RESULTS AND DISCUSSION

Graphene was synthesized by adapting a recent report of CVD synthesis on copper foil. After the synthesis, TEM samples were prepared via a recently developed direct transfer method. Atomic-resolution TEM imaging, electron diffraction, and Raman spectroscopy analysis confirmed that the graphene from this synthesis method is mostly single layer (see Supporting Information), in agreement with previous reports. STEM images demonstrate that graphene of large area (more than 20 μm × 20 μm) can be perfectly transferred to commercial TEM grids, with non-single-layer regions (including local folding structures) comprising less than 10% of the sample area (see Supporting Information).

Grains and GBs are identified using SED-STEM, which involves scanning a nanoparallel electron beam (NPEB) across a suspended graphene membrane in the diffraction mode of STEM. A related diffraction acquisition method with scanning micrometer-size beam has been previously used for domain mapping of polycrystalline films. When the electron beam laterally traverses a tilt GB, gradual transitions are observed from one hexagonal set diffraction to a relatively rotated set (Figure 1); each set results from an individual grain of single-layer graphene. Experimentally obtained graphene diffraction patterns at a transition are shown in Figure 1b–d. Diffraction patterns are acquired with a NPEB of 45 nm diameter. The hexagonal diffraction pattern (A spots) in Figure 1b transitions to a relatively rotated hexagonal pattern (B spots) in Figure 1d. There are intermediate locations in which both hexagonal patterns appear together in a single diffraction graph, as shown in Figure 1c. This occurs when the electron beam simultaneously probes both grains at the interface. Across the transition, the intensity profiles of diffraction A spots show an expected diminishing trend, and those of B spots show an expected intensifying trend, as the area of the associated grain (or number of carbon atoms in its associated graphene grain lattice) under the electron beam illumination, respectively, decreases or increases, as shown in Figure 1f.

Intensity variations of A spots, B spots, and their sum across the transition are shown in Figure 1f. Importantly, the intensity sum of A and B spots is nearly constant over the transition. This is compelling evidence that the transition is due to a tilt GB and not another microstructure, such as foldings or overlapping of two misoriented graphene sheets. Compared to single-layer graphene, such overlapping microstructures have multilayer regions and would therefore increase the effective area of crystalline graphene under electron illumination, which would lead to an increase of the intensity sum at a transition, contrary to observations.

The graphene grain’s lateral isolation in the sample plane also enables us to perform dark-field (DF) TEM imaging for facile GB identification in the case of highly rotated (>−10°) tilt GBs. Figure 2a shows a bright-field (BF) TEM image of graphene (prepared on a commercial Quantifoil holey carbon grid) where a diffraction transition occurs. There are no special features that appear to be GBs in the BF image. Figure 2b shows a diffraction pattern with two sets of hexagonal patterns at the transition, which are relatively rotated by 25.6°. We selectively obtain the bright contrast enhancement in one grain by transmitting only a single diffraction spot (marked with dotted circles c or d) with a small objective aperture. Figure 2c clearly reveals that the left side is brighter than the right side of the DF image, which is divided by a sharp line feature. The illumination change to the other transmitted diffraction spot produces a DF image with the inverted contrast in the graphene area (Figure 2d), while the line feature does not change. There is no overlap between the two bright regions in the two DF images (Figure 2c,d). This demonstrates that the line feature thus identified is a GB, not a local overlapping of two distinct graphene...
structures. We note that the GB is generally straight but changes its direction locally along the boundary in this magnification range.

We have used both SED-STEM and DF-TEM to map out graphene grains and their boundaries over a scale large enough to encompass multiple grains. In a pre-collected SED-STEM image, we mark and compile the locations where diffraction patterns make transitions for tracing a grain map. The DF technique can confirm this mapping process at high-angle GBs. Figure 3a shows a graphene GB map overlaid on the corresponding STEM image. The annotated angles inside each grain are the relative angles of the hexagonal diffraction pattern measured against a reference grain (overlaid in red) at the central region. We determine a graphene grain size in the range of 3–10 μm using our synthesis conditions. One should caution that identified grain boundaries in this study are restricted to the cases of tilt GBs. Even though nontilted GBs can exist in graphene, SED-STEM and DF-TEM methods are only applicable for visualizing tilt GBs in graphene. Aberration-corrected TEMs, which will be discussed later in this article, can be utilized to image nontilted GBs.

Macroscopic mapping of graphene GBs additionally allows us to systematically investigate the relative misorientation angles between adjacent grains (Figure 3b). A misorientation angle can be defined to be smaller than 30° in our study due to the hexagonal symmetry. It is found that significant portions of misorientations are located around 0° (low-angle tilt GB) and 30° (high-angle). The reported grain size of the polycrystalline copper used for our graphene synthesis is approximately 100 μm, which is much bigger than the graphene grain size we have found here. Hence, numerous graphene GB formations occur within a single copper grain. The high percentage of 0° and 30° misorientations implies that there are interactions from the copper substrate causing the preferential lattice alignment of graphene during the graphene synthesis. A related study correlating preferential growth directions of graphene with the crystalline direction of the underlying Cu(111) substrate has been recently reported. Further systematic study of graphene synthesis on single-crystal and polycrystalline copper will help in understanding graphene growth and substrate alignment.

Aberration-corrected TEMs have been used to image atomic defects on carbon nanotubes and graphene including vacancies and topological defects. Recently, there has been a report of GB-like structures in...
Figure 4. Atomic-resolution images of a high-angle tilt GB of graphene. (a) Atomic-resolution image of graphene GB. The left and right parts of the image are different tilt grains, which are relatively tilted by 26.6°. The red dashed rectangle is the field of view for panel d. The inset shows the Fourier transform of the image. It shows the two sets of hexagonal patterns from two grains. The scale bar is 2 nm. (b) Atomic-resolution image of the same region after removing one set of hexagonal patterns from the fast Fourier transform. The contrast of the right side of the image completely disappears, indicating that the graphene has no defects inside the right side grain. (c) Atomic-resolution image after removing another set of hexagonal patterns from the fast Fourier transform. The left side of the image disappears. (d) Zoom-in image of the high-angle tilt GB of graphene. The pentagon, hexagon, and heptagon are overlaid with red, black, and blue polygons, respectively. The GB shows an array of alternating pentagon and heptagon structures. The scale bar is 0.5 nm.

METHODS

Graphene Sample Preparation. Graphene is synthesized on 25 μm thick copper foil (99.9% Alfa Aesar, Ward Hill, Ma), following a recent report. After the synthesis, graphene is transferred to Quantifoil holey carbon TEM grids using a direct transfer method. In brief, we place the Quantifoil TEM grid onto a graphene-covered copper foil such that the Quantifoil carbon film side faces the graphene. Then we wet the sample with a drop of isopropyl alcohol and dry it with a home-built vacuum line to promote adhesion between the Quantifoil carbon film and the graphene. Heating the sample at 120 °C on a hot plate can produce better adhesion. The sample is placed into a solution of FeCl₃ to etch the underlying copper foil and is then rinsed in deionized water. Before putting TEM
samples into the microscope, the sample is heated at 180 °C for 10 min to remove adsorbates on the graphene surface. Diffraction Acquisition and Imaging. We use a Zeiss Libra 200F operated at 200 keV. The microscope optics use the nanoparallel electron beam (NPEB) setup optimized for fine diffraction pattern acquisition in STEM mode. In our work, we use two different configurations which give nanoparallel circular beams with diameters of 830 and 45 nm, respectively. The 45 nm beam is used for Figure 1 and Figure 3 grain mapping. The 830 nm beam is used for diffraction data in Figure 2 and Figure 3. All diffraction patterns are energy filtered with 40 eV width. Bright-field and dark-field TEM imaging is also performed using the same microscope in TEM imaging mode. Aberration-Corrected TEM. TEAM G5, operated at 80 keV, is used for atomic-resolution imaging of graphene grain boundaries. The low acceleration voltage minimizes the electron beam damage to the graphene samples. The microscope is tuned by the image Cs aberration corrector with a monochromated beam giving a spatial resolution of better than 1 Å, which enables us to resolve individual carbon atoms at the grain boundaries. Acknowledgment. We thank O. V. Yazyev and S. G. Louie for helpful discussions, and J. Yuk for technical assistance. This research was supported in part by the Director, Office of Energy Research, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH-11231 which provided for preliminary TEM and Raman characterization; by the National Science Foundation within the Center of Integrated Nanomechanical Systems, under Grant ECC-0832819, which provided for CVD graphene synthesis; and by the National Science Foundation under Grant No. 0906539 which provided for design of the experiment, suspended sample preparation, and analysis of the results. Portions of the present study were performed at the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, which is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. K.K. acknowledges additional support from a Samsung Scholarship, and W.R. acknowledges support through a National Science Foundation Graduate Research Fellowship. Supporting Information Available: Additional figures for characterization of single-layer CVD graphene samples, additional atomic-resolution TEM images of a tilt grain boundary, and a movie (real-time video recording) of graphene diffraction pattern transitions through grain boundaries in graphene. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES