A direct transfer of layer-area graphene

William Regan,[1,2] Nasim Alem,[1,2,3] Benjamín Alemán,[1,2,3] Baisong Geng,[1,4] Çağlar Girit,[1,2] Lorenzo Maserati,[1,5] Feng Wang,[1,2,3] Michael Crommie,[1,2,3] and A. Zettl[1,2,3,a]

[1]*Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA*
[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[3]*Center of Integrated Nanomechanical Systems (COINS), Berkeley, California 94720, USA*
[4]*School of Physical Science and Technology, Lanzhou University, Lanzhou 730000,
People's Republic of China*
[5]*Politecnico di Milano, 20133 Milano, Italy*

A facile method is reported for the direct (polymer-free) transfer of layer-area graphene from metal growth substrates to selected target substrates. The direct route, by avoiding several wet chemical steps and accompanying mechanical stresses and contamination common to all presently reported layer-area graphene transfer methods, enables fabrication of layer-area graphene devices with unprecedented quality. To demonstrate, we directly transfer layer-area graphene from Cu growth substrates to holey amorphous carbon transmission electron microscopy (TEM) grids, resulting in robust, clean, full-coverage graphene grids ideal for high resolution TEM. © *2010 American Institute of Physics*. [doi:10.1063/1.3337091]

Graphene, a single atomic monolayer of sp^2-bonded hexagonal carbon with extraordinary mechanical, electronic, and optical properties, has become a subject of great interest in materials science following its experimental isolation by the mechanical cleavage of graphite.[1,2] In the years since this development, more synthesis methods have emerged to isolate single to few layer graphene, such as epitaxial growth on SiC,[3,4] oxidative/thermal intercalation and ultrasonication of graphite,[5] and most recently by chemical vapor deposition on metal substrates such as Ni[6] and Cu.[7] In particular, Cu growth has garnered considerable interest due to its ability to produce macroscopic areas of mostly monolayer graphene, with domain sizes comparable to the size of the largest flakes that can be produced by mechanical exfoliation. In order for growth on Cu to be a viable route to large-scale graphene applications,[8] there must be a reliable method for transferring the graphene from metallic Cu substrates to more useful (e.g., insulating) substrates. To date, transfer of layer-area graphene has been achieved using a polymer coating—typically polymethyl methacrylate (PMMA) or polydimethylsiloxane (PDMS)—as a temporary rigid support during etching of the metal to prevent folding or tearing of the graphene.[6,7] Unfortunately, the use of these polymers necessitates several wet chemical steps that can contaminate and mechanically damage the graphene.

In this letter, a simple method is described for the direct transfer of layer-area graphene from Cu growth substrates to various target substrates. Surface tension and evaporation are used to pull Cu-supported graphene into intimate contact with the targets, simultaneously achieving the desired graphene/target bond and providing a rigid graphene support (the target substrate) during subsequent Cu etching.[9] This direct transfer is cleaner and gentler than polymer-based methods, making it ideal for the fabrication of a variety of optical, chemical, and electronic devices that utilize large, uniform graphene sheets.

As a demonstration of principle, we chose an amorphous carbon (a-C) transmission electron microscopy (TEM) grid—SPI Au Quantifoil with 1.2 micron holey a-C film—as the target substrate. However, as discussed below, other target substrates are possible. The structure of graphene makes it ideally suited for use as a TEM support.[9–13] Graphene is only a single carbon atom thick, an order of magnitude thinner than the best currently available amorphous TEM supports. This thinness and the low atomic number of carbon make graphene almost completely transparent to the electron beam. The slight beam interaction with the hexagonal carbon monolayer generates a well-defined signal that can be easily subtracted from resulting images and diffraction patterns. Somewhat counterintuitively, one can often achieve higher resolution images of a graphene-supported object than of a similar suspended object because, despite not being perfectly transparent to the electron beam, the graphene support helps dampen vibrations that would blur the suspended object. Graphene may therefore be the best possible TEM support for studying a variety of materials, namely, nanostructures and biological molecules that could otherwise not be resolved with conventional TEM supports.[10,11] While exfoliated graphene has been previously isolated on TEM grids,[9,10,12,13] these methods require delicate or cumbersome processing and limit the suspended graphene area to exfoliated flake sizes, 100 microns in diameter at most. Such a small target makes sample preparation difficult and unreliable. Thus, a reliable, clean transfer of layer-area graphene to TEM grids would be a significant advance for high resolution microscopy.

Figure 1 illustrates two routes, a standard polymer-based method (left) and our direct method (right), to transfer graphene from Cu growth substrates to TEM grids. Both transfers begin with layer-area graphene growth on a Cu foil—Alfa Aesar No. 13382, 25 microns thick—via low-pressure chemical vapor deposition.[7] A rigid support is needed to prevent destruction of the atomically thin graphene film during Cu etching. In the standard transfer, this support is a polymer, such as PMMA applied via spin-coating. In the

a)Electronic mail: azettl@physics.berkeley.edu.

Standard Transfer

graphene on Cu

Spin on and cure PMMA.

FeCl3 etch

DI rinse

Pull graphene on PMMA out of DI onto grid.

Lift off PMMA in acetone.

IPA rinse → poorly-adhered, dirty graphene grid

Direct Transfer

graphene on Cu

Place grid on graphene and drop on IPA. Grid binds to graphene as IPA evaporates.

FeCl3 etch

DI rinse

IPA rinse → well-adhered graphene grid

FIG. 1. (Color online) A comparison of the standard (e.g., PMMA) and direct transfer of layer-area graphene to holey a-C TEM grids.
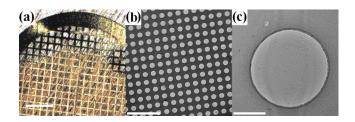

FIG. 2. (Color online) (a) Optical microscopy showing nearly complete adhesion (top edge not yet adhered) between the TEM grid's a-C film and the graphene on Cu, shown during the evaporative sticking process. Scale =0.5 mm. (b) Portion of a grid frame showing large-domain, clean graphene sheets with some cracks and folds. Scale=10 μm. (c) Clean, single grain graphene covering a-C hole. Scale=0.5 μm.
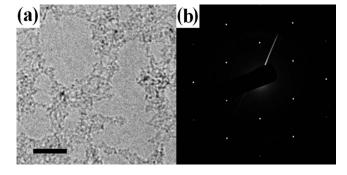

FIG. 3. (a) A typical image of a low-defect region with large atomically clean areas. Scale=25 nm. (b) SAD of this region showing the hexagonal structure of the (0001) basal plane. Tilt measurements performed in this region yielded invariant diffraction intensities, a strong indicator of monolayer graphene.

floating the sample on a solution of aqueous FeCl$_3$ (0.1 g/mL) for approximately 2 h. After Cu etching, the direct transfer process is complete. The sample, now referred to as a graphene TEM grid, is floated on de-ionized (DI) water and rinsed in IPA to wash off remaining Cu etchant, remove organics, and encourage effective drying. The standard transfer, however, requires several additional steps which damage and contaminate the graphene. After removal of the Cu, the delicate PMMA/graphene film is transferred to a DI bath to wash off remaining etchant and then extracted from the DI bath by pulling it out onto the target TEM grid. Finally, the PMMA is removed with acetone and the sample is rinsed in IPA. In short, the direct transfer process is much cleaner than the standard polymer transfer as it involves fewer potential contaminants (PMMA, acetone). Additionally, by anchoring the grid's a-C film to the graphene in the initial wet step, the direct transfer process avoids mechanical damage suffered during wet transfers of the graphene/PMMA film, producing a much more robust graphene TEM grid than the standard polymer transfer.

Characterization of direct transfer graphene TEM grids is performed on a JEOL 2010 TEM operated at 100 kV. Figure 2 shows the graphene grid at different magnifications. Macroscopic grid-wide graphene coverage is apparent in Fig. 2(a), an optical micrograph captured near the end of the evaporative adhesion step. Darker regions in this image show where graphene has bonded to the a-C support. Figure 2(b), a subset of a grid frame captured by TEM, reveals large unperturbed graphene sheets with occasional folds and cracks. Figure 2(c) shows a higher magnification image of a single graphene domain covering an a-C hole. Figure 3(a) shows a typical view of the suspended graphene, with large (tens of nanometers) atomically clean regions separated by scattered amorphous and/or organic materials covering the highly reactive graphene surface, rivaling the cleanliness seen earlier with exfoliated graphene flakes transferred to TEM grids.[10] We detect no evidence of polycrystalline Cu residue on the surface, suggesting a complete and clean etch. Selected area diffraction (SAD) of the region in Fig. 3(a) is shown in Fig. 3(b), revealing the distinctive hexagonal structure of graphene. The invariant intensity of the diffraction pattern during tilting gives unambiguous evidence that the membrane is indeed a single layer.[12,14]

Figure 4(a) reveals a fold or grain boundary. Folds are commonly seen in metal-based layer-area graphene growth, possibly forming to relieve stress during the cooling of the

direct transfer, this support is provided by the target substrate, specifically the TEM grid's a-C film. To bond the graphene and a-C, the TEM grid is placed on top of graphene on Cu and a drop of isopropanol (IPA) is gently placed on top of the grid to wet both the grid's a-C film and the underlying graphene film. As the IPA evaporates, surface tension draws the graphene and a-C together into intimate contact.[9] (To achieve strong adhesion, the evaporative surface tension must be strong enough to slightly warp either the Cu foil or the target substrate, so care must be taken when choosing Cu foil and target thickness.) The completeness of the adhesion between the graphene and a-C can be confirmed by optical microscopy, as optical interference effects give a noticeable contrast difference between adhered and nonadhered regions. Figure 2(a) shows a grid near the end of this evaporative process, when all but the top portion of the grid has been adhered onto the graphene on Cu. A 10 to 20 min bake on a hot plate at 120 °C helps to evaporate any remaining IPA and strengthen the graphene/a-C bond. The next step in both transfer processes is to etch away the Cu foil, achieved by
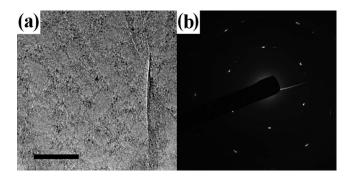
FIG. 4. (a) A region with a fold or grain boundary in the graphene. Scale =50 nm. (b) SAD of this region showing the hexagonal graphene structure, with small and large angle separation of diffraction spots due to sheet misalignments resulting from the fold or grain boundary.

graphene and metal from the high synthesis temperature down to room temperature. The corresponding SAD in Fig. 4(b) again shows the characteristic hexagonal structure of this region. The large and small angle separation of the diffraction spots results from the sheet misalignment caused by the fold or grain boundary.

As shown, optical microscopy and TEM confirm that our direct transfer results in complete grid coverage, a strong bond between the grid support film and the graphene, and a highly uncontaminated graphene surface, making the graphene TEM grid well suited for high resolution TEM. The resulting grid is substantially easier to work with than previous grids made with exfoliated flakes.[9,10,12,13] Millimeter-scale graphene coverage avoids the need for precise aiming when preparing graphene-supported samples, and grid preparation is fast and reliable. Additionally, target materials besides holey a-C are compatible with this technique. We have achieved graphene transfers to different materials with varied geometries, including Au gilder fine bar TEM grids, Au TEM grids with lacey carbon, formvar-coated Quantifoil grids, and plastic transparency film. Although not a necessary condition, it appears that perforated target geometries improve the efficacy of the transfer process, perhaps as a result of variations in surface tension forces near perforations and/or solvent evaporation pathways through the target. Beyond producing excellent graphene TEM grids, our clean, gentle graphene transfer technique may facilitate a multitude of graphene studies and applications in such areas as hydrogen storage, gas sensing, electrochemistry, catalysis, and other advanced electrical/optical fields.

[1]K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).
[2]Y. Zhang, J. P. Small, W. V. Pontius, and P. Kim, Appl. Phys. Lett. **86**, 073104 (2005).
[3]C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, J. Phys. Chem. B **108**, 19912 (2004).
[4]E. Rollings, G.-H. Gweon, S. Zhou, B. Mun, J. McChesney, B. Hussain, A. Fedorov, P. First, W. de Heer, and A. Lanzara, J. Phys. Chem. Solids **67**, 2172 (2006).
[5]M. J. McAllister, J.-L. Li, D. H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme, and I. A. Aksay, Chem. Mater. **19**, 4396 (2007).
[6]A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, Nano Lett. **9**, 30 (2009).
[7]X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, Science **324**, 1312 (2009).
[8]A. K. Geim, Science **324**, 1530 (2009).
[9]J. C. Meyer, Ç. Ö. Girit, M. F. Crommie, and A. Zettl, Appl. Phys. Lett. **92**, 123110 (2008).
[10]J. C. Meyer, Ç. Ö. Girit, M. F. Crommie, and A. Zettl, Nature (London) **454**, 319 (2008).
[11]M. D. Fischbein and M. Drndić, Appl. Phys. Lett. **93**, 113107 (2008).
[12]J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, D. Obergfell, S. Roth, Ç. Girit, and A. Zettl, Solid State Commun. **143**, 101 (2007).
[13]T. J. Booth, P. Blake, R. R. Nair, D. Jiang, E. W. Hill, U. Bangert, A. Bleloch, M. Gass, K. S. Novoselov, M. I. Katsnelson, and A. K. Geim, Nano Lett. **8**, 2442 (2008).
[14]J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth, Nature (London) **446**, 60 (2007).