

## Hydrocarbon lithography on graphene membranes

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We present a simple and efficient way to obtain freestanding graphene membranes. On these membranes, we demonstrate that electron-beam induced deposition of carbon can be used to obtain arbitrary patterns with a nanometer-scale resolution. In the case of a periodic grating, we obtain a half-pitch of 2.5 nm. Electron-beam induced deposition on graphene might be used to create nanometer-scale doping patterns, diffraction gratings, or etch masks in this novel electronic material. © 2008 American Institute of Physics. [DOI: 10.1063/1.2901147]

Since its isolation in 2004 (Ref. 1 and 2) and the experimental verification, the following year of many of its theoretically predicted electronic properties,<sup>3,4</sup> single- and few-layer graphene has been suggested as a promising candidate material for future microelectronic devices. It is a ballistic conductor with a long mean free path,<sup>1,3,4</sup> can behave as a semiconductor if shaped into a ribbon,<sup>5-7</sup> can be locally gated,<sup>8</sup> and can carry spin currents<sup>9</sup> (even at room temperature<sup>10</sup>) and supercurrents.<sup>11</sup> Graphene is in many respects similar to carbon nanotubes but expectations are that for various applications, graphene will be easier to control. This is partly because it can be patterned into arbitrary shapes by lithographic means<sup>12</sup> which readily provides a degree of control that is difficult to achieve with nanotubes.

Nevertheless, smaller devices require not only novel materials but also a means of shaping those materials into a tiny circuit. State of the art, resist based, electron-beam lithography (EBL) methods, have enabled few-nanometer feature sizes, such as isolated lines with about 5 nm width<sup>13-16</sup> or 2 nm wide gaps.<sup>17</sup> In case of periodic structures, however, the smallest demonstrated resolution of EBL is about 15 nm half-pitch (30 nm periodicity).<sup>14,15,18</sup> Indeed, it has been argued in Ref. 19 that resist-based EBL on a substrate is inherently limited to around 20 nm half-pitch for periodic patterns. Although electron beams can be focused to subangstrom diameters,<sup>20</sup> scattered and secondary electrons generated in a bulk substrate and resist limit the modulation in the energy profile that can ultimately be realized.

Direct-write, electron-beam induced deposition (EBID) has been previously used to define nanometer-scale structures, with a half-pitch of periodic gratings down to 1.6 nm.<sup>21</sup> These have been demonstrated on amorphous carbon films<sup>22</sup> and silicon nitride membranes<sup>21</sup> with thicknesses of 10 and 30 nm, respectively. It has also been demonstrated that a range of materials other than amorphous carbon can be deposited by careful control of the precursor.<sup>21-27</sup> In fact, calculations in Ref. 28 show that this high-resolution should be possible by EBID on any thickness of substrate; however, the tails of deposited spots (deposited material outside of the beam) is suppressed on ultrathin membranes. Our membranes are another one to two orders of magnitude thinner than previously studied membranes, thereby reducing the effects of secondary and scattered electrons even further. We

present here a direct-write deposition of arbitrary patterns on suspended graphene membranes with a resolution (half-pitch) of 2.5 nm. We find that our minimum feature size corresponds to the diameter of the focused electron beam and observe no deposition outside the deposited structures.

The most important difference between using an amorphous film substrate and graphene for patterning is that graphene has remarkable electronic properties that can be significantly altered directly by doping, shaping, or defect generation. By using graphene membranes, we directly pattern the material that is likely to be used in a host of next generation electronic devices. These patterns could readily serve as an etch mask,<sup>29</sup> or to create a doping pattern. In addition, we expect that the arbitrary design of local perturbations with nanometer precision will allow a wide range of experiments that explore the scattering and diffraction of relativistic quasiparticles. To facilitate our high-resolution patterning method, we have developed a simple and efficient process to obtain freestanding graphene membranes.

Our experimental procedure begins with graphene flakes made by the established “scotch tape” method<sup>1-4</sup> on a bulk substrate. In order to obtain freestanding membranes, we have developed transfer processes of the graphene flakes to commercially available electron microscopy grids. Three methods for the transfer are described below. We have used Quantifoil perforated carbon films with 1.3  $\mu\text{m}$  holes on 200 mesh gold grids (Quantifoil Micro Tools GmbH, Jena, Germany) for all three methods and also C-flat perforated carbon films with 1  $\mu\text{m}$  holes on 200 mesh gold grids (Protochips Inc., Raleigh, NC) for the third approach.

In the first method, we start with graphene flakes on a silicon substrate with a 300 nm silicon dioxide layer. We identify graphene flakes by optical microscopy [Fig. 1(a)], and place the Quantifoil grid onto the flake. A small drop of isopropanol is added [Fig. 1(b)] and left to evaporate. The surface tension of this solvent during evaporation pulls the perforated carbon film into contact with the substrate and graphene flakes [Fig. 1(c)]. To improve the adhesion, we now heat the sample on a hot plate at 200 °C for 5 min. After cooling, we place the substrate with the now well-sticking transmission electron microscopy (TEM) grid into a 30% solution of semiconductor grade potassium hydroxide at room temperature. The silicon dioxide layer is slowly etched by the potassium hydroxide and the TEM grid along with the graphene sheets falls off after a time ranging from a few minutes to a few hours. It is then transferred without drying

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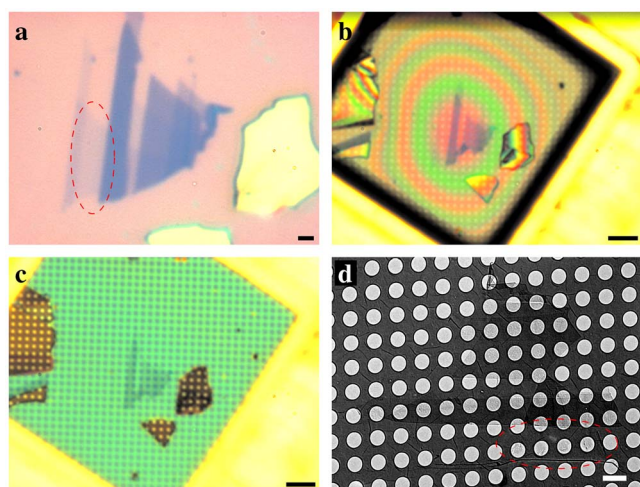


FIG. 1. (Color online) Preparation of graphene membranes. (a) Optical micrograph of a flake on a Si/SiO<sub>2</sub> substrate. (b) Quantifoil grid on top of the graphene flake, immersed in isopropanol. Color rings appear just before the liquid is completely evaporated as the perforated carbon film is pulled into contact with the surface. (c) Quantifoil (with perforated carbon film) on the graphene flake. (d) Free hanging flake (low-magnification TEM image) after release from the substrate. The red circle in (a) and (d) indicates the single-layer region of this sample. Scale bars are (a) 2  $\mu\text{m}$ , [(b) and (c)] 10  $\mu\text{m}$ , and (d) 5  $\mu\text{m}$ .

into a water bath and, subsequently, to isopropanol. Finally, the sample is carefully dried in air. The single- and few-layer graphene sheets remain suspended across the holes of the Quantifoil grid.

In the second method, we begin with graphene flakes prepared on silicon substrates with a 300 nm silicon dioxide layer and a 10–30 nm layer of polymethylmetacrylate. Again, the Quantifoil TEM grid is placed onto the flakes and pulled into contact with the surface by evaporation of a solvent (isopropanol). Contact is improved by heating on a hot plate. The top layer of the substrate is now dissolved in a bath of acetone or methylpyrrolidone. After the TEM grids with the graphene flakes separate from the substrate, they are again transferred to isopropanol before drying. This second method avoids the use of acids or bases (such as potassium hydroxide).

The third and most simple approach is as follows. The TEM grid with the perforated carbon film is placed onto a graphene flake and pulled into contact by a drop of isopropanol, as before (using a Si/SiO<sub>2</sub> substrate). After it has fully evaporated, a second drop of isopropanol is carefully placed on the substrate, not on top but next to the TEM grid. As the drop expands and wets the entire substrate, the liquid squeezes in between the TEM grid and the substrate, lifts the TEM grid, and separates it from the substrate again. The grids with the perforated carbon films end up suspended on the liquid surface. About 25% of the single- and few-layer graphene flakes stick to the TEM grid as it separates from the substrate, which is then picked up with tweezers and dried in air. In spite of some loss of graphene sheets, we find that due to its simplicity, this last process is the most efficient one in terms of graphene membranes obtained in a given amount of time. In addition, it avoids the use of any polymers, acids, or bases and the graphene sheet only comes into contact with the silicon dioxide, isopropanol, and possibly some scotch tape residue.

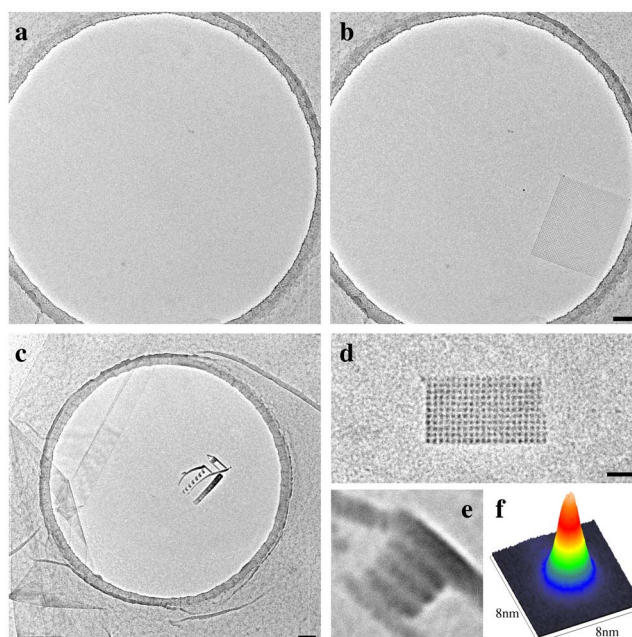


FIG. 2. (Color online) (a) A freestanding membrane spanning a 1.3  $\mu\text{m}$  hole in the TEM grid. (b) The same membrane after electron-beam induced deposition of a dot array on part of the area. (c) Lawrence Berkeley National Laboratory logo written onto graphene. (d) Pattern with 2.5 nm half-pitch (5 nm dot separation). (e) Lines in the logo (windows of the clock tower at top right) spaced 6 nm apart. (f) Intensity profile of the electron beam that was used to write these structures. Scale bars: [(b) and (c)] 100 nm and (d) 20 nm.

Just before insertion into the TEM, the graphene membrane samples are again heated on a hot plate to reduce the amount of adsorbates that are present on the sample surface due to the wet preparation and due to air exposure. For the results shown here, samples were heated for 10 min at 200 °C. Again, care must be taken as too much heat causes the graphene sheets to detach from the amorphous carbon films and collapse into a crumpled shape. We clearly observe that the heat treatment reduces the rate of carbon deposition in EBID, which makes it easier to control at the expense of a longer writing time.

We use a JEOL 2010 TEM operated at 100 kV to write the patterns. A small beam is formed in the convergent-beam diffraction mode of the illumination system, with a full width at half maximum of 2.5 nm and a total current of approximately 1 pA [Fig. 2(f)]. The advantage of using a TEM for this process is that the shape and size of the beam can be directly observed; however, we note that a nanometer-sized beam can be generated with any high quality scanning electron microscopy and lithography system as well. By employing a computer controlled movement of the electron beam, arbitrary patterns are created. In contrast to the “digital” nature of resist-based lithography, we have here a continuous “gray scale” control of the deposited amount of material. Figures 2(a) and 2(b) show the same graphene membrane before and after writing a periodic dot array. Figure 2(c) shows a different membrane with a nonperiodic pattern, the logo of the Lawrence Berkeley National Laboratory. The windows of the clock tower on the rightmost part of the pattern are spaced only 10 nm apart [Fig. 2(e)]. The smallest carbon pattern we obtained in this way is a dot array with a spacing of 5 nm (i.e. a half-pitch of 2.5 nm), as shown in Fig. 2(d). Here, the dwell time at each point was one second.

The precursors in the EBID process are hydrocarbons adsorbed on the sample surface, as evidenced by the fact that the amount and time of heating the sample before insertion into the TEM strongly affects the deposition rate. The heating reduces the EBID rate (increases write time) but makes it more controllable for smallest structures. Damage to the graphene sheet by the electron beam is unlikely, as the dose of  $10^4 e^-/\text{\AA}^2$  at 100 kV in the exposed areas is only 1/1000 of the dose that was found to cause significant damage in single-walled carbon nanotubes.<sup>30</sup>

The above results demonstrate a means to create arbitrary shapes on single- and few-layer graphene membranes with a resolution of 2.5 nm with continuous control over the amount of deposited material. This is a resolution that, by extrapolating from the international technology roadmap for semiconductors (ITRS), will be the DRAM half-pitch in the year 2034.<sup>31</sup> Indeed, if we consider the dots in Fig. 2(d) as bits for data storage, we have an extremely high information density per volume due to the ultrathin substrate (we estimate the height of the dots at 5 nm). However, it must be noted that long write times, in our case 1 bit/s, are a well known drawback of EBID direct-write lithography.

Given the high sensitivity of graphene's electronic properties to small-scale perturbations,<sup>32</sup> our deposited material will have a significant effect on the local electronic structure of the graphene membrane. An individual deposited dot will thus act as a spatially controlled scattering center. It is then easy to conceive of waveguide and optics analogies, e.g., a diffraction grating, for the electron waves. Indeed, the dimensions of our structures are only a few multiples of the Fermi wavelength of the electrons in graphene of 0.74 nm.<sup>33</sup> We anticipate that, in particular, the ability to also create nonperiodic arbitrary shapes will lead to a wide range of interesting experiments. As previously mentioned, it has also been demonstrated that, by a suitable choice of the precursor, a wide range of materials other than carbon can be deposited by EBID.<sup>21–27</sup> In this way, it should be possible to create specific doping patterns on graphene. In addition, EBID-deposited amorphous carbon can be used as an etch mask<sup>29</sup> pointing to a way to “cut out” a preselected structure from a graphene sheet.

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