Transfer Printing of Graphene Using Gold Film

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ABSTRACT We report a facile transfer printing process for easily exfoliating prepatterned graphene from HOPG surfaces by using gold film as the transfer stamp. The transferred printed patterns consist of single- and few-layer graphene with macroscopic continuity. Raman spectra show that some defects appear along the edges of the graphene patterns, which were induced by the oxygen plasma-etching treatment of the HOPG surface. This transfer-printing technique paves a new and simple way to get large-scale graphene patterns on to any substrates.

KEYWORDS: graphene · transfer print · Raman spectrum

Highly oriented pyrolytic graphite (HOPG) is one of the best sources for high crystallinity graphene layers.[1] Graphene, a popular material of recent times, is a single layer of graphite and a perfect 2D crystalline material with very high electron mobility and other interesting properties. Graphene has become an ideal object for both fundamental studies[2−4] and future electronic applications.[5,6] During last several years, there have been many efforts for exfoliating HOPG into multiple layers and even to obtain monolayer graphene, such as *via* chemical exfoliation,[7,8] mechanical cleavage,[9−11] and electrostatic force based separation.[12,13] By improving the micromechanical cleavage technique, Novoselov *et al.* fixed graphite onto a substrate with glue and then used a tape to repeatedly peel off graphene.[9] They found that individual single- and few-layer graphene could be successfully isolated from graphite by the repeated peeling-off process. Most recently, Liang *et al.* used a stamp with thousands of pillars to choose cut graphene islands from graphite.[12] By applying voltage between graphite and the substrate, they found that the graphene islands could be exfoliated onto a silicon wafer by electrostatic force.[13] However, there are still issues to be resolved in order to easily manipulate and transfer graphene on a large scale.

Recently, gold has been used to remove as-grown carbon nanotubes from silicon substrate through the strong adhesion between gold and carbon nanotubes.[14,15] In this report, we use gold film as a transfer stamp to exfoliate prefabricated graphene patterns from the HOPG surface. The exfoliated graphene patterns are thus successfully transfer-printed onto substrates. We found that most of these transfer-printed graphene patterns consist of just a few graphene layers with macroscopic continuity. Some defects appear along the edges of the graphene patterns, which were induced by the oxygen plasma-etching of the HOPG surface. This new and facile transfer-printing technique allows us to manipulate and transfer few-graphene layers over large areas, without exposing to any glue, giving the process a clear advantage to print graphene patterns for electronic applications.

RESULTS AND DISCUSSION

Figure 1 shows the schematic flowchart of the transfer-printed graphene patterns through gold-stamp-assisted exfoliation. First, micrometer-scale line features with different sizes were patterned on the surface of a HOPG disk by using photolithographic techniques followed by an oxygen plasma-etching process, as shown in schematic flowchart (*i*).[16] Figure 1a shows an optical microscopy image of 10 μm line patterns fabricated on the HOPG surface. Atomic force microscopy (AFM) shows that the thickness of these graphene line patterns is around 10 nm after etched by O_2 plasma for 30 s. Second, 500 nm gold film was deposited onto the patterned HOPG disk surface, and a thermal releasing tape (Revalpha tape from Nitto Denko) was used to peel off the gold film together with the

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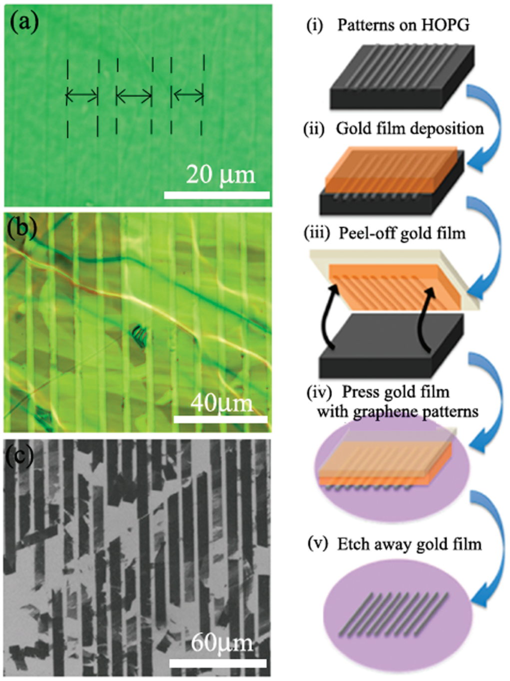

Figure 1. Schematic diagram and photographs of transfer-printed graphene patterns by gold-film-assisted exfoliation. The process includes (*i*) fabricating graphene patterns on HOPG by photolithography and O_2 plasma etching, (*ii*) depositing gold film on the patterns, (*iii*) peeling off the gold film with graphene patterns, (*iv*) transfer-printing graphene patterns onto any substrates, and (*v*) etching away the gold film. (a,b) Optical microscopy images of graphene patterns on HOPG surface and gold film, respectively. Dashed lines and arrows are used to highlight the line patterns. (c) Scanning electron microscopy (SEM) image of graphene patterns transfer-printed onto a silicon substrate with 300 nm thermal SiO_2.

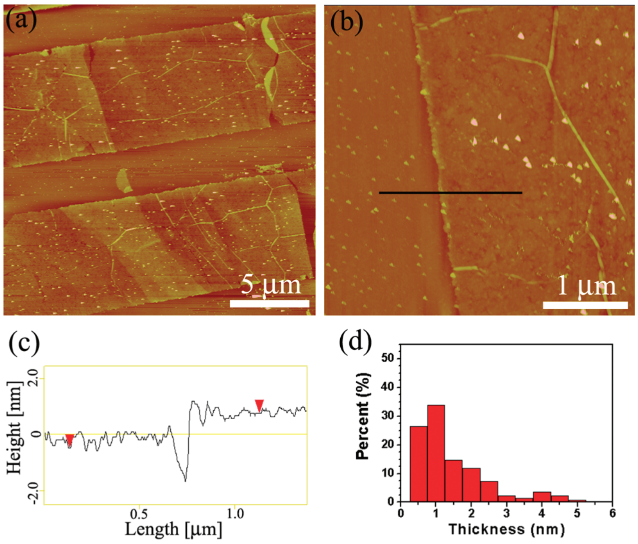

Figure 2. (a) Low- and (b) high-magnification atomic force microscopy (AFM) images of transfer-printed graphene with 10 µm line patterns exfoliated and printed on a silicon substrate. The solid line indicates a scanning trace across the transfer-printed graphene, which is plotted in (c). (d) Histogram shows the average graphene thickness data collected from 200 transfer-printed graphene patterns, showing that the majority of the transferred graphene is very thin, including the monolayer.

graphene patterns, as shown in schematic flowcharts (*ii*) and (*iii*). Figure 1b clearly shows an optical image of peeled-off graphene patterns that were attached on the gold film. In order to isolate some residual multigraphene layers from the transferred graphene patterns, we use another new thermal tape to gently peel off the obtained film for several times. Finally, as shown in schematic flowcharts (*iv*) and (*v*), the gold film with graphene patterns was pressed onto any target substrate preheated on a hot plate at 180 °C. During this process, the thermal tape was released and removed from the gold film. After this, gold etchant solution (from Transene) was used to etch away the gold film, leaving only graphene patterns on the target substrates. Figure 1c shows a scanning electron microscopy (SEM) image of 10 µm line graphene patterns transfer-printed on silicon wafer, which revealed that our transfer-printing technique could easily transfer graphene patterns over large areas. We suggest that the strong adhesion between gold and carbon surface acts as one kind of clamp to transfer prepatterned graphene layers. The following heat-transfer process will make graphene patterns tightly attach to the substrate.

Atomic force microscopy was performed on our samples for detecting the average thickness of the transfer-printed graphene patterns. Figure 2a,b shows the low- and high-magnification AFM images of 10 µm line graphene patterns, which were exfoliated and transfer-printed on silicon substrate. The AFM image clearly displays a variation of graphene thickness over the printed line patterns. Some ripples can be seen on the graphene surface, as a result of the exfoliation and printing process. Many particles are residual gold particles left on the graphene, which can be removed by quick supersonic treatment. The line scan denoted by the solid line and accordingly plotted in Figure 2c explicitly exhibits the variation of the graphene thickness from 0.8 to 2.5 nm. The histogram in Figure 2d shows the average thickness of transfer-printed graphene, suggesting that most of the transferred graphene in the patterns has a thickness of about 1−3 nm, which amounts to less than 10 graphene layers.[17,18]

Raman spectrum of the transferred graphene was measured by a Renishaw spectrometer under 514 nm laser excitation at room temperature. Figure 3 shows that these spectra manifest three intense features, which is the D peak at a Raman shift of ~1360 cm^{-1}, the G peak at ~1585 cm^{-1}, and the 2D band at ~2700 cm^{-1}.[19−23] Figure 3a compares the Raman spectra that were recorded from different regions of transferred graphene patterns in Figure 3b. The intensity of the D peak increases when the Raman spot was focused on the edge of the graphene pattern (position 1), indicating some disorder introduced at the patterned edges of graphene during the O_2 plasma-etching process.[16,19] The G peak and 2D peaks of graphene are due to the doubly degenerate zone center E_{2g} mode and the second order of zone-boundary phonons.[20,21] It is found that the 2D peak position taken from the center regions of the transferred graphene (position 2 at 2714 cm^{-1}, position 3 at 2707 cm^{-1}) was down-shifted 15−25 cm^{-1} with respect to that of position 1 (2730 cm^{-1}), while the G peak position is 2−5 cm^{-1} higher. Compared to bulk graphite, monolayer and few-layer graphenes have a much sharper and downshifted 2D band, and their G band position increases with the number of layers decreasing.[22−25] The shift of G and 2D peak positions suggests that most of our transfer-printed graphene patterns contain only a few layers of graphene, which is consistent with our AFM results.

CONCLUSION

In summary, we have developed a new and simple way for exfoliating and transfer-printing graphene patterns from the HOPG surface onto substrates by using gold film as a transfer stamp. AFM and Raman spectroscopy results indicate most of these transfer-printed patterns have a thickness of just a few graphene layers. This transfer-printing approach prevents pristine graphene patterns from potential chemical contamination and could serve as an alternative solution for printing graphene electrical circuits on large scales.[26]

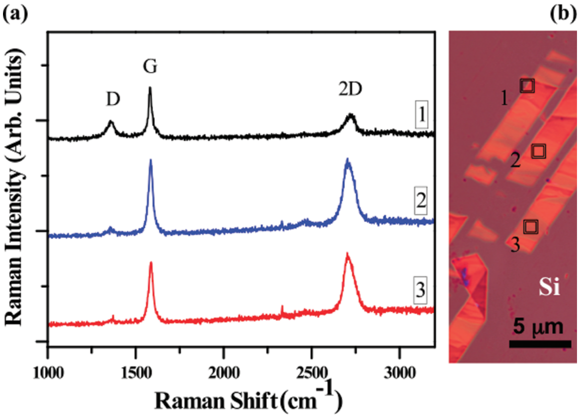

Figure 3. (a) Raman spectra of transfer-printed graphene on silicon substrate, which were recorded from different regions described in the optical image (b).

EXPERIMENTAL METHODS

Fabrication of Patterns on HOPG: A commercial HOPG disk (from Mikro-Masch) was cleaned and cleaved to get a fresh flat surface. Photoresist S1813 was coated on those fresh HOPG surfaces by 3000 rpm/min for 45 s. As followed, a general photolithography process was carried out to fabricate line patterns with different sizes. The prepatterned sample was placed into the oxygen plasma setup (FISCHIONE, Plasma Cleaner Model 1020) to etch line patterns on the HOPG surface.

Gold Film Deposition and Patterns Transfer: A sputter facility (TORR International Inc., CrC-150 Sputtering System) was used to deposit 500 nm thick gold on the prepatterned HOPG disk surface. A thermal releasing tape (Revalpha tape from Nitto Denko) was pressed onto the HOPG disk for 1 min and gently peeled off. Those prefabricated graphene patterns were directly exfoliated from the HOPG disk by the above gold film.

Print of Patterns on Target: A silicon wafer was cleaned and placed on a hot plate at 180 °C for 5 min. The gold film with graphene patterns was pressed onto this target substrate for 2 min. During this process, the thermal tape was released and removed from the gold film. In order to remove the gold film, the substrate was gently immersed into a gold etchant solution ($KI-I_2$ complex, from Transene) for 2 h at room temperature. Finally, gold film was etched away, leaving only graphene patterns on the substrate.

Scanning electron microscopy (JEOL 6500), Raman spectroscopy (RENISHAW InVia Raman Microscope), and atomic force microscopy (NanoScope *III*a, Digtal Instruments) were used for sample's characterization.

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