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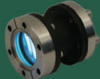
Frame assisted H$_2$O electrolysis induced H$_2$ bubbling transfer of large area graphene grown by chemical vapor deposition on Cu

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An improved technique for transferring large area graphene grown by chemical vapor deposition on copper is presented. It is based on mechanical separation of the graphene/copper by H$_2$ bubbles during H$_2$O electrolysis, which only takes a few tens of seconds while leaving the copper cathode intact. A semi-rigid plastic frame in combination with thin polymer layer span on graphene gives a convenient way of handling- and avoiding wrinkles and holes in graphene. Optical and electrical characterizations prove the graphene quality is better than that obtained by traditional wet etching transfer. This technique appears to be highly reproducible and cost efficient. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4775583]

Graphene, a two-dimensional material formed from a hexagonal lattice of sp^2 carbon atoms, has been identified as a promising candidate in several applications ranging from beyond-CMOS technology[1] to deoxyribonucleic acid (DNA) sequencing.[2] This is due to its impressive properties, such as extremely high intrinsic mobility for both electrons and holes,[3,4] high transparency,[5] high thermal conductivity,[6] large tensile strength,[7] etc. For some time, however, problems in scaling, reproducibility and uniformity of the techniques used for graphene production, and subsequent transfer to various target substrates have limited its use in industry. Chemical vapor deposition (CVD) is the most promising methods for graphene synthesis. It is feasible for large scale production of uniform graphene in an industrial-friendly fashion.[8–15] Also, it has been demonstrated that the quality of CVD graphene grown on catalytic metals is good enough to be used in optoelectronics where transparency and conductivity are equally important.[16]

A bottleneck of the CVD technique, however, is the graphene transfer from metals to foreign substrates; a direct growth of graphene on insulators is not yet mature.[17–20] Commonly, graphene is supported by a polymeric film while the metal is removed.[8–15] The resultant polymer/graphene complex is then placed on the target after which the polymer is removed by a solvent. In this process, the graphene is exposed to metal etchant for a great many hours, which may induce defects and/or excess doping. Also, the handling and cleaning of the fragile material once metal is etched away is not easy; folding or rapture of graphene is often seen. The so-called roll-to-roll printing process alleviates the problem and gains more reproducibility.[9] Still, the pressure homogeneity and therefore the graphene adhesion to substrate is hard to maintain uniform over large areas during stamping. Most importantly, however, the expensive high purity metal catalysts are etched away, increasing cost of the graphene industrial production.

Very recently, Cheng et al.[21] have suggested a transfer technique based on the mechanical separation of graphene from Pt foils by H$_2$ bubble formation at the cathode of an electrolytic cell. The catalyst is not consumed and can be used repeatedly. To date, however, there are no detailed reports on the generalized transfer technology for the most common catalyst in CVD graphene: copper, despite a combined effort of wet etching and electrochemical separation.[22] In this letter, we present an electrolysis bubbling-assisted transfer of graphene grown by CVD on Cu. The metal is not consumed, proving the method to be cost-efficient for real applications. Furthermore, we ease manipulation of graphene by using a plastic frame attached to the polymer/graphene prior to separation from copper. The frame also alleviates the effect of turbulence during the bubbling. Altogether, this results in much fewer wrinkles and holes in the transferred graphene. The process is accomplished in a few tens of seconds, producing material comparable or better than the graphene transferred by wet etching of Cu,[15,23] as characterized by optical and electrical means.

For the graphene synthesis, 50 μm thick 99.99% pure Cu foils and a cold-wall low-pressure CVD reactor (Black Magic, AIXTRON) are used. After standard cleaning, the Cu foil is heated to ~1000 °C and annealed for 5 min with a flow of 20 sccm H$_2$ and 1000 sccm Ar. Then, 30 sccm prediluted CH$_4$ (5% in Ar) is used during another 5 min as the

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carbon source. After the growth, the system is evacuated to <0.1 mbar and cooled. The process is reported in greater detail in our previous publication.[15]

A schematic representation of the graphene transfer process can be seen in Fig. 1. In this work, spin coated poly(methyl methacrylate) (PMMA) (2000 rpm, 5 min cure at 160 °C) is used as the supporting polymer thin film. The graphene on the bottom face of the foil is dry etched by O_2 plasma (graphene is usually formed on both sides of the metal foil). For simplicity, we remove the bottom graphene in this letter. However, we can simultaneously isolate two graphene films from both sides of Cu as well, doubling the yield, which is impossible to achieve in the wet etching based technology. For the supporting frame, we opted to use 100-200 μm thick polyethylene terephthalate (PET) (see Fig. 2(a)), even though any semi-rigid plastics that are inert during the electrolysis would be suitable. Many glues (e.g., epoxy) that remain sticky in wet environments could be used to attach the frame to the PMMA/graphene/Cu-sandwich. However, we found that PMMA itself (drop coated onto the frame that was going to be in contact with the PMMA/graphene/Cu complex, 160 °C cure) was the cleanest and most efficient choice. The gluing was carried out also at 160 °C on a hot plate, well above the glass transition temperature of PMMA ($T_g \approx 105$ °C).

The frame/PMMA/graphene/Cu-bundle is then used as the cathode of an electrolytic cell with 0.25 M NaOH aqueous solution electrolyte. For the anode, a platinum electrode is used (see Fig. 1(b)). To start the process, the current is ramped to ~1 A and maintained at that level until the graphene is completely separated from the Cu foil by the H_2 bubbling. The typical time required for separation is ~30 s. Subsequently, the frame/PMMA/graphene-bundle is picked up and rinsed in several deionized water baths (Fig. 2(b)). It
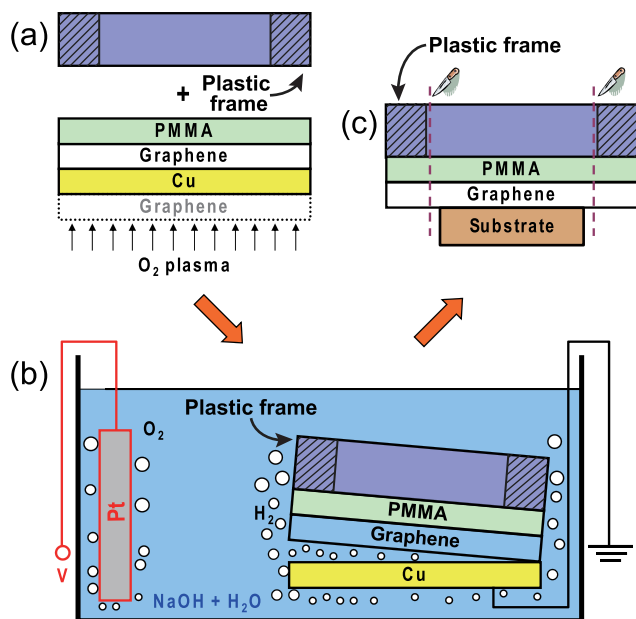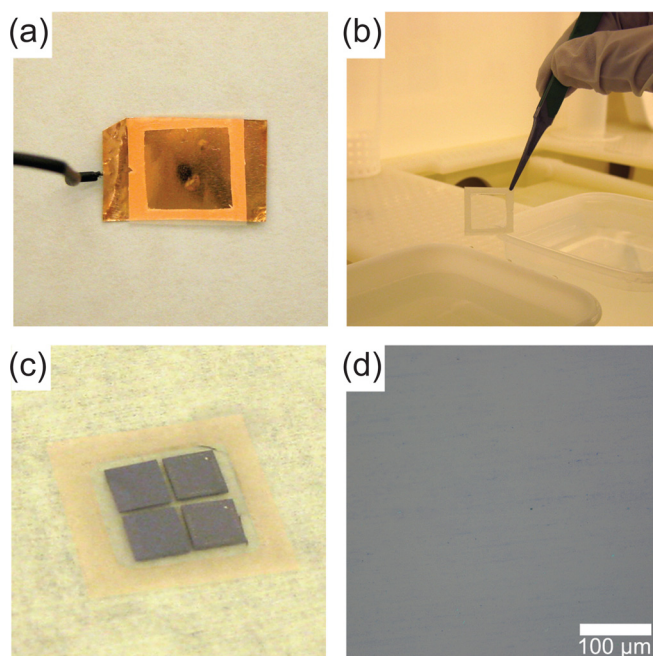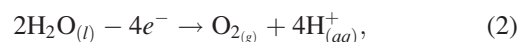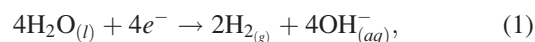

FIG. 2. Images of different stages in the graphene transfer technique. (a) Frame on the PMMA/graphene/Cu complex. (b) Detached frame/PMMA/graphene dipping into water for cleaning. (c) Simultaneous transfer to 4 target substrates (6 × 6 mm²). (d) Optical microscope image of the transferred graphene film on 300 nm SiO_2/Si. Video of the bubbling transfer is available online.[24]

is then placed on the target substrates (e.g., Si with 300 nm SiO_2) and left at room temperature until it gets dry. It is remarkable to notice that the graphene film can be transferred to several substrates at once (Fig. 2(c)). The frame is easily removed simply by cutting through the PMMA at the inside borders (Fig. 1(c)); it can be reused many times. Afterwards, the samples are baked at 160 °C for 5 min to remove water residue and improve adhesion before the PMMA is dissolved by acetone. By repeating the procedure, multiple layers of graphene can also be deposited, as discussed in more detail in the supplementary material.[24]

Gas bubbles are known to be very effective in separating solid layers uniformly. For example, in commercial silicon on insulator (SOI) technology, hydrogen bubbles are used to separate ultra-thin silicon film (commonly known as "smart cut") for the transfer to a handle wafer. Here, we use H_2 bubbling to isolate graphene because other common gases such as O_2 and Cl_2 (anode products) may oxidize graphene. Furthermore, if Cu is used as the anode, it may be electrochemically oxidized and etched. The half equations of the reactions at our cathode (Eq. (1)) and anode (Eq. (2)) of the cell are

$$4H_2O_{(l)} + 4e^- \rightarrow 2H_{2(g)} + 4OH^-_{(aq)}, \tag{1}$$

$$2H_2O_{(l)} - 4e^- \rightarrow O_{2(g)} + 4H^+_{(aq)}, \tag{2}$$

respectively. Obviously, the NaOH electrolyte is only used to enhance the electrical conductivity of water. The absence of Na^+ in the essential reaction is ensured by its very negative standard electrode potential of $E^0 = -2.71$ V. Note that many electrolyte solutions can be used for bubbling transfer

FIG. 1. Schematic illustration of the frame assisted H_2 bubbling transfer. (a) Deposition of the PET frame on top of the sample and etching of the graphene at the unprotected side of Cu with O_2 plasma. (b) H_2 bubbling separation of the frame/PMMA/graphene from the Cu foil induced by H_2O electrolysis. (c) Frame removal after transfer.

of graphene, such as Na_2SO_4. We have also found that a lower concentration of NaOH leads to a cleaner graphene surface; $\sim$0.25 M NaOH is identified as providing the best balance between graphene quality and effective bubble production. More details can be seen in the supplementary material.[24]

In our experiments, we have found that the H_2 bubbles can detach most foreign materials (including graphene, PMMA, etc.) that are loosely bound to the metal surface. This might cause some difficulties when transferring graphene grown on evaporated Cu thin films on SiO_2/Si. Due to the weak bonding to the substrate, the Cu thin film becomes separate both from the graphene and the underlying SiO_2/Si, making the thin-film recycling difficult unless an appropriate adhesion metal layer is used when depositing the copper thin film. We also notice that tightly bonded materials (e.g., native oxide of Cu) are usually difficult to detach. Finally, we stress that the plastic frame is important to preserve a smooth graphene surface. Intensive H_2 bubbles create considerable turbulence, often resulting in broken or severely corrugated graphene if not using the frame.

The inset of Fig. 3 demonstrates an electron diffraction pattern of the as-grown graphene obtained in transmission electron microscope (TEM). The diffraction dots with six-fold symmetry and their equal intensity clearly indicate high quality monolayer graphene. Fig. 2(d) shows a typical optical image of the graphene electrochemically transferred to SiO_2/Si wafer. The graphene is seen to be very uniform and smooth. Fig. 4(a) shows the Raman spectrum measured after the transfer. The 2D/G peak ratio is as high as $\sim$2.3. The full width half maximum (FWHM) of the 2D peak is 32.4 cm^{-1}. This confirms the existence of single layer graphene.[8–15] A very small D/G peak ratio of 0.13 indicates that the amount of defects introduced by the transfer technique is negligible. For optical transparency analysis, the graphene is transferred to microscope glass slide. The transmittance for the single layer and artificial bilayer graphene (two step transfer) are shown in Fig. 4(b). By subtracting the effect from the glass
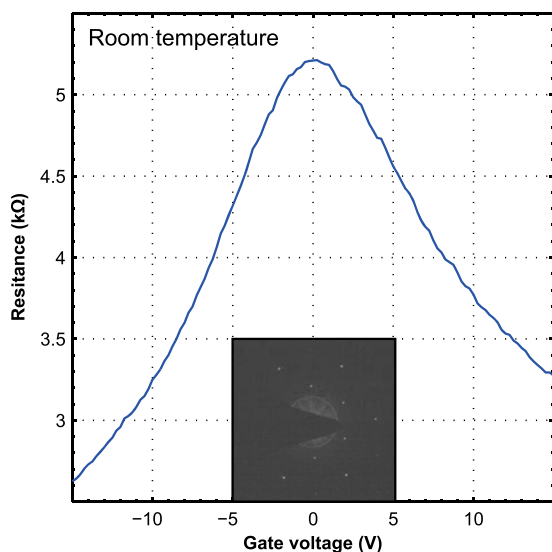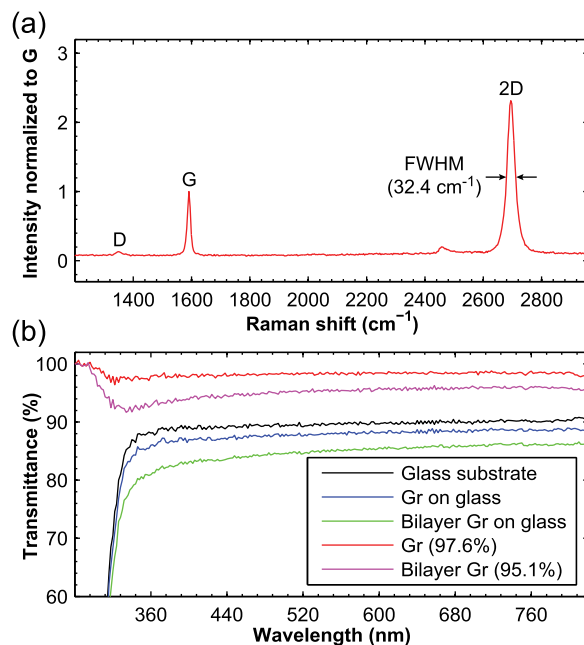
FIG. 4. Optical characteristics of the as-transferred graphene. (a) Raman spectrum (514.5 nm) of the graphene transferred to SiO_2/Si. (b) Optical transmittance of a single layer and a bilayer graphene film transferred to glass substrates. The transmittance for monolayer and bilayer graphene is extracted from the measured values by subtracting the substrate absorption. Gr denotes graphene.

substrate, single and double layer graphene films show transmittance of 97.6% and 95.1%, respectively, in good agreement with the expected values.[5]

Transistor devices are fabricated by a two-step electron beam patterning (in the channels and Ti/Au electrodes, respectively) of the graphene transferred on Si wafers with 300 nm thermal oxide. The resistance of the graphene device is measured at ambient conditions as a function of the back gate voltage, V_G, which is applied to the conducting Si substrate (see Fig. 3). Following the model previously reported in literature,[25] the field-effect carrier mobility is estimated to be about 2000 cm^2 V^{-1} s^{-1}. It is worth noting that no special treatments (vacuum or current annealing, etc.) have been carried out before the electrical characterization. The results are comparable or better than those achieved in our traditional wet etching graphene transfer.[15,23,24]

In summary, an electrochemical technique to transfer graphene grown on Cu has been proposed. Using Cu as the cathode, the graphene can be readily detached from the metal by H_2 bubbling resulting from H_2O electrolysis. The catalyst remains unconsumed (except for the native oxide removal prior to CVD) and can be reused many times, thereby drastically reducing the material cost of graphene synthesis. Another innovative aspect is the use of a semi-rigid frame, supporting the polymer/graphene bundle all the time, reducing the amount of wrinkles/holes and making the technique reproducible and robust. Optical and electrical characterizations suggest that the quality of graphene is similar or better than that attained by traditional etching-based transfer methods, but at a much higher efficiency and lower cost.

FIG. 3. Device resistance as a function of the gate voltage V_G for field effect mobility measurement. In the inset, an electron diffraction pattern of the monolayer graphene film is shown.

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