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Graphene transfer: key for applications

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The first micrometer-sized graphene flakes extracted from graphite demonstrated outstanding electrical, mechanical and chemical properties, but they were too small for practical applications. However, the recent advances in graphene synthesis and transfer techniques have enabled various macroscopic applications such as transparent electrodes for touch screens and light-emitting diodes (LEDs) and thin-film transistors for flexible electronics in particular. With such exciting potential, a great deal of effort has been put towards producing larger size graphene in the hopes of industrializing graphene production. Little less than a decade after the first discovery, graphene now can be synthesized up to 30 inches in its diagonal size using chemical vapour deposition methods. In making this possible, it was not only the advances in the synthesis techniques but also the transfer methods that deliver graphene onto target substrates without significant mechanical damage. In this article, the recent advancements in transferring graphene to arbitrary substrates will be extensively reviewed. The methods are categorized into mechanical exfoliation, polymer-assisted transfer, continuous transfer by roll-to-roll process, and transfer-free techniques including direct synthesis on insulating substrates.

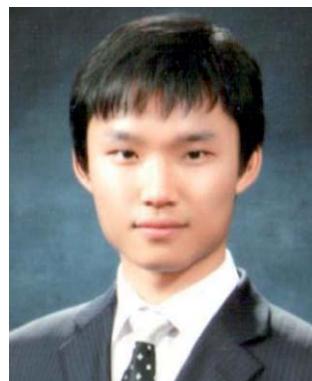
Introduction

Graphene has been in the spotlight since its isolation and the discovery of its fascinating properties. Phrases such as the first two-dimensional material,^{1,2} single atomic thickness,¹ incredible carrier mobility,^{3–5} and mechanical strength,⁶ have become the defining words for graphene during the past decade. Rapid scientific studies on graphene physics and chemistry have revealed a vast number of possible applications in fields from electronics to biomedicine,^{7,8} to energy storage/conversion

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(supercapacitors,^{9,10} batteries,^{11,12} fuel cells,^{13,14} and solar cells^{15–19}). The road to application, however, is not so simple. Shortly after the discovery of graphene by mechanical exfoliation¹ (Scotch tape method), one after another different synthesis methods such as chemical exfoliation,^{20–23} epitaxial growth^{24,25} and chemical vapor deposition (CVD),^{26–28} were developed to improve the graphene quality and to produce it at a large scale. Fine tuning of growth conditions, careful selection of substrate catalyst and the development of the CVD method that succeeded in growing a 30 inch graphene sheet have brought graphene research one step closer to industrial applications.²⁹ Nevertheless, synthesis of a single uniform graphene sheet still remains a significant challenge, let alone the consistent reproduction of high quality graphene. Although quality improvements can be made during the synthesis steps,^{30–34} it is important to note that most of the time degradation of quality occurs during the transfer process due to tearing and ripping of the graphene sheets.^{35,36} There may be more merit in reducing the degradation during transfer than making other improvements. However, amidst the many improved and innovative synthesis methods reported, graphene transfer has not received the attention it is due.

This article intends to extensively review graphene transfer methods and explore what advancements have been recently developed to minimize the transfer damage.

Transfer techniques for graphene sheets

1. Mechanical exfoliation

The very first graphene sheet was obtained by exfoliating a thin piece of graphite from highly oriented pyrolytic graphite (HOPG) with Scotch tape.¹ Since graphite is a stacked 3-dimensional structure of graphene, repeatedly peeling the layers with Scotch tape eventually yielded a very thin piece of graphite, which could then be rubbed onto a silicon wafer to produce a mixture of few-layer and single-layer graphene flakes as shown in Fig. 1. More delicate methods that later emerged attached HOPG at the tip of an AFM silicon cantilever and operated the

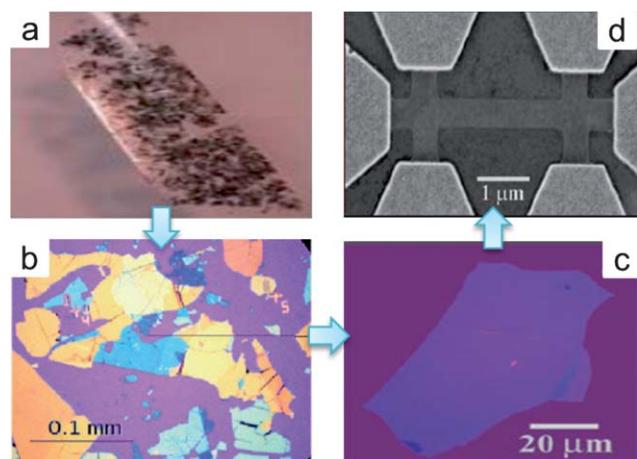


Fig. 1 Mechanical exfoliation of a graphene flake from HOPG using Scotch tape. (a) An image of graphene flakes on scotch tape. (b) Optical microscopy image of graphene flakes on SiO₂/Si wafer. (c) Optical microscopy image of relatively large few layer graphene flake on SiO₂/Si wafer. (d) Scanning electron microscope image of devices based on a patterned graphene flake. Reproduced from ref. 1 with permission from the American Association for the Advancement of Science Copyright 2004.

AFM in contact mode,³⁷ which is essentially dragging it across the Si-wafer just like drawing with a pencil. This method also yielded graphene flakes with varying numbers of layers. These two earlier methods of acquiring graphene do not quite fit in as transfer steps; these “mechanical exfoliations” were the only means of both graphene obtainment (rather than synthesis) and transfer.

Graphene exfoliated from HOPG is of high quality and its crystal structure is well-ordered, as the name suggests.^{1,4,38,39} However, with the Scotch tape and AFM method, the lateral size of the graphene is limited to a few micrometers and the thickness varies vastly from 10 to 100 nm. Although single layer graphene is visible on the Si-wafer due to its optical properties, the nanoscale size of the flakes makes it extremely difficult to locate



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single-layer graphene,⁴⁰ which is the desired type for research purposes, amidst the much more abundant multi-layered sections. The few that were found by researchers revealed the graphene band-gap structure as well as its fascinating electrical and physical properties.^{1,4,41} Graphene, behaving as a massless dirac fermion,⁴² was reported to have carrier mobilities of $\sim 15\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$,⁴³ with carriers moving almost ballistically.^{44,45} It is optically transparent⁴⁶ and has a Young's modulus of $\sim 1\text{ TPa}$.⁶ These characteristics of graphene caught the interest of many researchers as it showed potential for many different applications, such as transparent electrodes,^{47–52} barriers,^{53–55} and sensors.^{56,57} The potential for applications, however, called for graphene sized well beyond a few micrometers.

One of the solutions to produce larger graphene sheets was epitaxial growth on SiC. It was already well known that thermal decomposition of SiC grows layer of graphite on the surface.^{24,25,58} It also grows homogeneous, single-crystalline graphene epitaxial to the underlying SiC.^{24,59,60} With the realization that free-standing 2D graphene sheets could exist, researchers controlled the content of carbon in SiC and growth condition to reduce graphite production and grow thinner layers.^{61,62} Although during the initial period of development the studies on epitaxial graphene were conducted directly on top of a SiC substrate, development of a transfer step soon followed. The new exfoliation methods that followed graphene growth on SiC (as well as CVD growth) are independent transfer steps that differ from the previous mechanical exfoliation by Scotch tape or AFM drawing.

The Rogers group of the University of Illinois successfully transferred graphene from SiC to a target substrate using a bilayer film of gold and polyimide (PI).⁶³ Fig. 2a–c shows 100 nm thick Au deposited on graphene with electron beam evaporation, and PI applied by spin coating an amic acid solution and baking at 110 °C. The PI/Au/graphene layer was gently lifted from the SiC and delivered to a target substrate. Here, PI mainly

functioned as a mechanical support during transfer for the thin Au and graphene layers. The transferred graphene had a few holes and exhibited a high Raman defect peak (D peak, $\sim 1380\text{ cm}^{-1}$), but it was good enough to fabricate a back gated field-effect transistor with ambipolar characteristics and hole mobility of $\sim 100\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. The Rogers group later improved the graphene quality further by replacing Au with Pd and by employing a multi-stacking strategy, which reduces the degrading effects of holes and tears by layering several graphene sheets together (Fig. 2d–f).⁶⁴

A similar exfoliation transfer using thermal release tape was developed by Caldwell *et al.*⁶⁵ Holes approximately 10 µm in size were created during the transfer but the graphene showed a relatively small Raman D peak. Unlike the Raman studies, however, it was apparent from the comparison of before and after measurements of carrier density that the electrical properties were significantly decreased because of the holes and damage; the average mobility dropped from $1485\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ to $201\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ after the transfer. The transferred graphene was multilayer because of the high efficiency of thermal release tape in lifting off graphene from SiC substrate. While a complete and thorough transfer may be beneficial in certain applications, it is not helpful in getting few- or single-layer graphene. There also was an effort to exfoliate SiC graphene with Scotch tape but it brought back the same problem of producing small flakes and the difficulty of locating a single layer graphene flake.⁶⁶

For large scale graphene synthesis, a CVD method similar to that used for the synthesis of CNTs⁶⁷ rose in prominence as a more affordable alternative to SiC epitaxial growth. In CVD synthesis of graphene, a carbon precursor gas (typically methane) is provided in high temperature and low pressure conditions, and goes through a catalytic decomposition reaction on either Ni^{26,27} or Cu²⁸ catalyst metal. It is theorized that freed carbon atoms dissolve and segregate as graphene on Ni surface,^{26,68–70} and adsorb and reassemble into graphene on a Cu

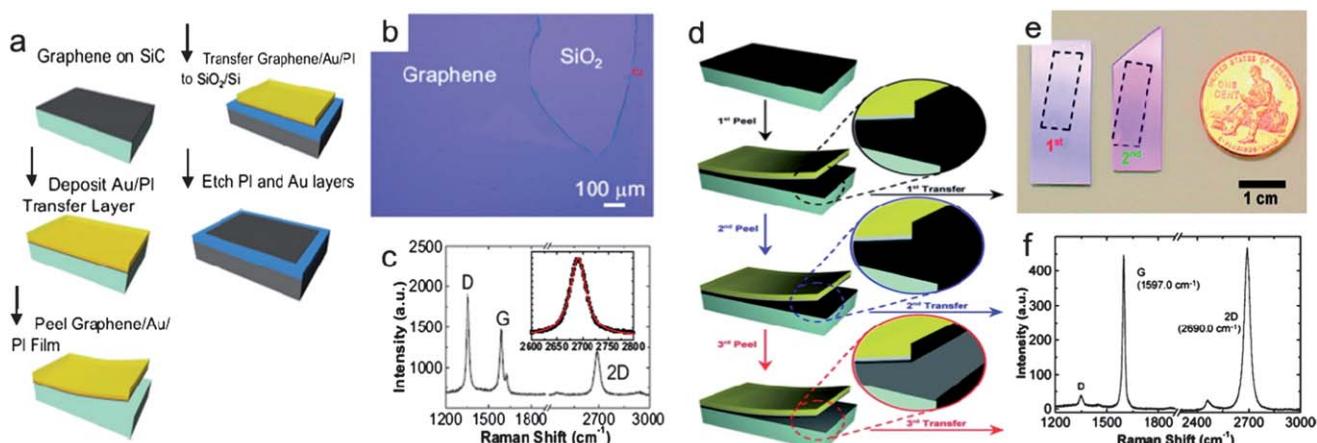


Fig. 2 Transferring graphene grown on a SiC wafer to another substrate using metal–polymer bilayer films. (a) Schematic illustration of the steps for transferring graphene on SiC wafer to another substrate. (b) Optical microscopy image of graphene film covering square millimetres of area. (c) Raman spectrum of graphene transferred on a SiO₂/Si wafer, showing the D, G, and 2D peaks that suggest multilayer graphene. Reproduced from ref. 63 with permission from the American Institute of Physics Copyright 2009. (d) Schematic illustration of procedures for layer-by-layer transfer of graphene grown on the SiC wafer to another substrate. (e) Photograph image of two transferred graphene films with square centimetre areas. (f) Raman spectrum of graphene transferred on a SiO₂/Si wafer, showing the D, G, and 2D peaks. Reproduced from ref. 64 with permission from the American Chemical Society Copyright 2010.

surface,⁶⁸ although the exact mechanism is still debated.³¹ Epitaxial growth of graphene on other metal surfaces has been tried (*i.e.* Ir,⁷¹ Ru,⁷² etc.), but Ni and Cu are preferred as they are the most economical metal substrates. As with graphene synthesis on SiC, a transfer step is required for CVD synthesis in order to separate graphene from the catalyst metal that it grew on and move it to an arbitrary substrate. As discussed in detail below, the most widely used transfer method for CVD synthesis is polymer-supported metal etching and transfer. The lack of a harsh peeling process results in superior graphene quality when compared to graphene exfoliated from SiC. However, some of the most recent work shows adaptation of the mechanical exfoliation transfer to CVD grown graphene.

The merit of mechanical exfoliation or peeling of graphene is most apparent in that chemical etching can be avoided. Typical etchants of Ni and Cu, such as iron nitrate,³⁵ iron chloride,²⁶ and ammonium persulfate,²⁹ are harsh and environmentally hazardous or expensive to dispose. With the research results that show the chemical doping effect⁷³ and damage done to graphene by etchants, skipping etching entirely seems even more favourable. For example, Lock *et al.* demonstrated the use of an azide-based linker molecule for CVD graphene exfoliation transfer (Fig. 3).⁷⁴ The linker molecules, *N*-ethylamino-4-azidotetrafluorobenzoate (TFPA-NH₂), were deposited on an oxygen plasma-treated polystyrene substrate. When attached to graphene and applied with heat and pressure, the linker molecules form strong covalent carbone bonds, enabling the clean removal of graphene from the catalyst metal. Another similar method developed by Yoon *et al.* used a thin layer of epoxy to peel off

graphene as shown in Fig. 4.⁷⁵ While doing so, they also measured and compared the adhesion energy of graphene on Cu metal ($0.72 \pm 0.07 \text{ J m}^{-2}$), which is larger than graphene on a silicon wafer ($0.45 \pm 0.02 \text{ J m}^{-2}$).⁷⁶

Because the process is etch-free, the Cu substrate can be reused many times for graphene growth without significant degradation of quality. Both of these CVD exfoliation methods require a substance to act as a “glue” to attach the graphene to the desired substrate. However, neither of the transfer methods include steps that remove these glue substances. Unless the desired end use of the prepared graphene is unaffected by the presence of these extra substances, development of ways to remove them seems essential for widespread use of the exfoliation transfer.

2 Polymer supported etching and transfer

Polymer supported transfer methods are being developed along with and specifically for CVD graphene synthesis, with a few exceptions where a polymer support is used for HOPG⁷⁷ or graphene oxide (GO)⁷⁸ film transfer. The metal substrate that graphene is synthesized on is used for catalytic purposes and is typically unwanted after the synthesis is complete so the removal of the metal is the logical step after the growth. Ni and Cu metals can be etched away in Fe(NO₃)₃, FeCl₃ or (NH₄)₂S₂O₈ and etching can be done without the support of polymers. For example, the Hong group reported wet etching transfer of CVD graphene (grown on Ni deposited on SiO₂/Si) in which an SiO₂ layer and Ni are etched in BOE and FeCl₃ solution and graphene is separated and scooped up on a substrate.²⁶ However, the ultrathin graphene is too prone to ripping and tearing during etching and transfer could, depending on the synthesis

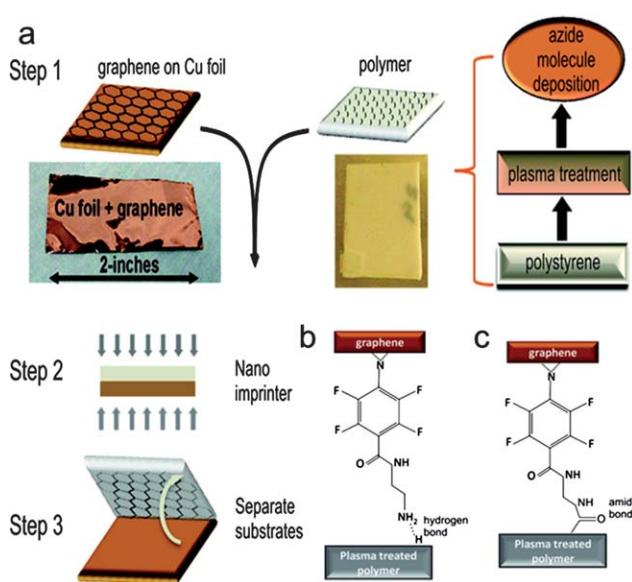


Fig. 3 CVD graphene transfer from Cu foil to a polymeric substrate using azide-based linker molecule. (a) Schematic illustration of the transfer procedures including polymer coating, imprinting, and separating from the Cu foil. Attachment schematic: (b) (PS H) hydrogen bond attachment between the TFPA and the hydroxyls/carboxyl groups of the plasma treated polystyrene surface; (c) (PS R) covalent bond attachment between the TFPA and the plasma treated polystyrene surface. Reproduced from ref. 74 with permission from the American Chemical Society Copyright 2012.

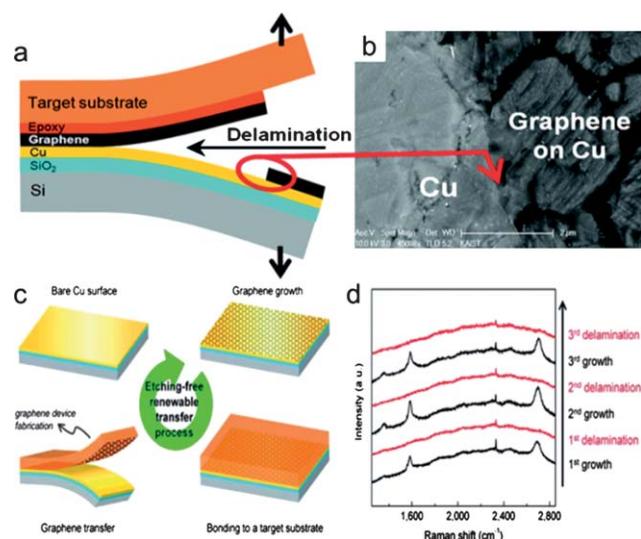


Fig. 4 Etching-free selective mechanical transfer of large-area monolayer graphene. (a) Illustration of graphene transfer using the mechanical delamination process. (b) High-magnification SEM image of interface between graphene on Cu and graphene-delaminated bare Cu. (c) Schematic of the steps of the etching-free renewable graphene transfer process. (d) Raman spectra of the synthesized graphene and graphene-delaminated bare Cu. Reproduced from ref. 75 with permission from the American Chemical Society Copyright 2012.

quality of a particular graphene, break apart even with the slightest disturbance. Therefore, many researchers, including the Hong group, who also reported polymer support transfer along with the dry transfer technique,²⁹ prefer the use of polymer support to ensure a safe transfer. In addition, the polymer support made transfer of large area graphene possible as synthesizable CVD graphene area increased rapidly to several inches in lateral width.

PDMS (polydimethylsiloxane) was one of the first polymers to be used for CVD graphene transfer. PDMS is durable, unreactive, moldable, resistant to many solvents, and it is the material of choice for soft lithography.⁷⁹ However, its most significant quality is the low surface free energy.⁸⁰ In soft lithography, the substance to be lithographed or “stamped” onto a substrate is applied to PDMS cast into the desired shape and pattern.⁸¹ Due to the low adhesion force that PDMS maintains with the substance, when the substance comes into contact with the target substrate it prefers to adhere to the substrate rather than the PDMS, thereby being released from PDMS and stamped onto the substrate. This same mechanism applies for graphene transfer.²⁶ Once PDMS (not necessarily patterned in this case) is brought into contact with graphene on a metal substrate, it acts as mechanical support until the metal etching is complete. After this step, when the freed graphene on PDMS is brought onto a substrate, typically SiO₂/Si or PET, the soft lithography principle applies; graphene is released from PDMS and transferred to the substrate with relatively higher surface free energy. Fig. 5 shows the schematic process of the PDMS transfer.

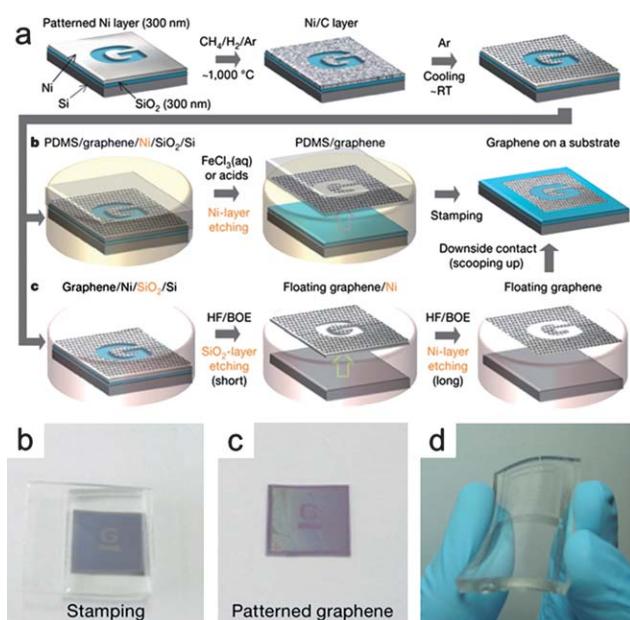


Fig. 5 A dry transfer process for a graphene film grown on an Ni film using a soft substrate, PDMS. (a) Schematic illustration of synthesis, etching and transfer processes for patterned graphene films using a PDMS stamp. (b-d) Photograph images of graphene films. (b) Attaching the PDMS on a SiO₂ substrate. (c) Peeling the stamp and leaving the graphene film on the SiO₂ substrate. (d) Graphene electrode for transparent and flexible electronics fabricated by using patterning method. Reproduced from ref. 26 with permission from the Nature Publishing Group Copyright 2009.

During the early days of CVD synthesis, one of the disadvantages of using PDMS transfer was the long etching time. Before large area graphene synthesis on Cu foil was realized CVD growth was conducted in small scales on SiO₂/Si wafers with catalyst metal deposition. Thus when PDMS was applied to the graphene/metal/wafer and submerged in etchant, only a thin layer of metal around the sides was exposed to the etchant. With such low contact area, etching is excruciatingly slow, often taking more than tens of hours. As the size of the wafer used to grow graphene increased, etching time became a major hindrance. In an effort to reduce the etching time, Lee *et al.* proposed the inclusion of a light ultra-sonication step, which gently releases the SiO₂/Si wafer from PDMS/graphene/metal layers.⁸² The separation from the wafer exposed the entire side of the metal surface to the etchant and significantly reduced the etching time.

Among the useful polymer supports, PDMS is especially apt for graphene device making. Delicately patterned graphene grown on a pre-patterned metal may require great care not to rupture it during transfer, but with PDMS stamping nano fabrication is made relatively simple. Fig. 6 shows the successful device manufacture using PDMS reported by Kang *et al.* Instead of growing patterned graphene, they molded PDMS with the desired pattern on one surface.⁸³ After the metal etching process, only the graphene resting on the protruded PDMS pattern remained. The graphene was stamped onto a device substrate and was used as an electrode for an organic field-effect transistor. With rubrene single crystal used as an active channel, the device showed an on-off ratio of ~10⁷ and field effect mobility of ~10 cm² V⁻¹ s⁻¹.

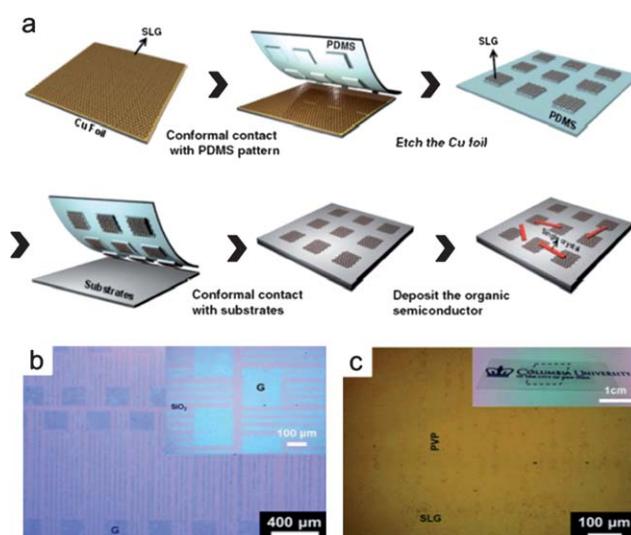


Fig. 6 The patterning and transferring of CVD-grown graphene using a micro-patterned elastomeric stamp. (a) Schematic illustrations of the micro-patterned graphene device fabrication for organic field effect transistor using rubrene single crystal semi-conductor. (b–c) Optical microscope images of patterned graphene electrodes using a stamping method. (b) Single layer graphene transferred on a SiO₂/Si wafer. The insert of (b) shows a magnified optical microscope image of micro-patterned graphene. (c) Single layer graphene transferred on PVP substrate. The insert of (c) is a photograph of transferred graphene on a transparent PET substrate. Reproduced from ref. 83 with permission from WILEY-VCH Verlag GmbH & Co. KGaA Copyright 2011.

PMMA (polymethyl methacrylate) is another widely used polymer support for CVD graphene transfer. It had already shown its usefulness in transferring films of CNTs⁸⁴ and a similar transfer method was adopted for graphene transfer. Unlike PDMS, which maintains weak van der Waals forces with graphene, PMMA coating forms covalent bonds with graphene. PMMA can be easily spin coated on graphene grown on any substrate and moved to any desired substrate. As Jing Kong's group reported, the initial PMMA transfer method was fairly simple: PMMA is spin coated on to graphene grown on metal²⁷ (or HOPG flakes on SiO₂/Si⁷⁷), the metal (or SiO₂) is then etched to free the PMMA/graphene layer and is scooped up on a desired substrate, lastly, the PMMA layer is washed in acetone (Fig. 7). Many reported experiments approved adequate transfer using PMMA for both thick graphene grown on Ni and monolayer graphene grown on Cu.

However, it was found that PMMA could cause cracks and tears in weak monolayer graphene. The Ruoff group judged that as the PMMA coating on graphene is dried, it holds the graphene rigid, keeping the ripples and folds on graphene that may have formed during the growth and cooling process.²⁸ These ripples can hinder good contact between graphene and the transfer substrate, causing graphene to tear off as the PMMA layer is washed away. In order to prevent this from happening, the group proposed applying a second layer of PMMA coating before washing off the first PMMA layer.³⁵ Fig. 8 shows the process of transfer of graphene film using PMMA double coating. Doing so re-dissolves the dried PMMA layer and relaxes the rigid form of graphene, allowing it to snuggly rest on the substrate with better

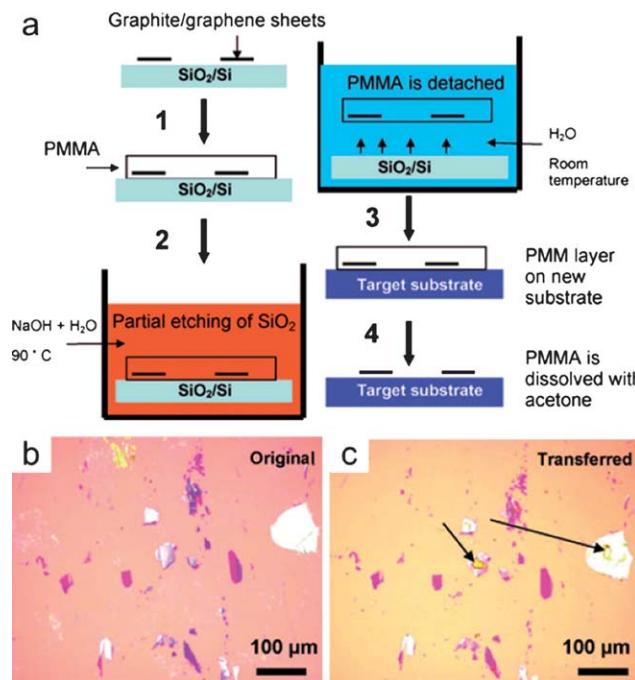


Fig. 7 Transferring single- and few-layer graphene flakes using PMMA. (a) Schematic illustration of the transfer procedures for graphite/graphene sheets. (b and c) Optical microscopy images of graphite and graphene pieces on the original (b) and the transferred (c) SiO₂/Si wafer. Reproduced from ref. 77 with permission from the American Chemical Society Copyright 2008.

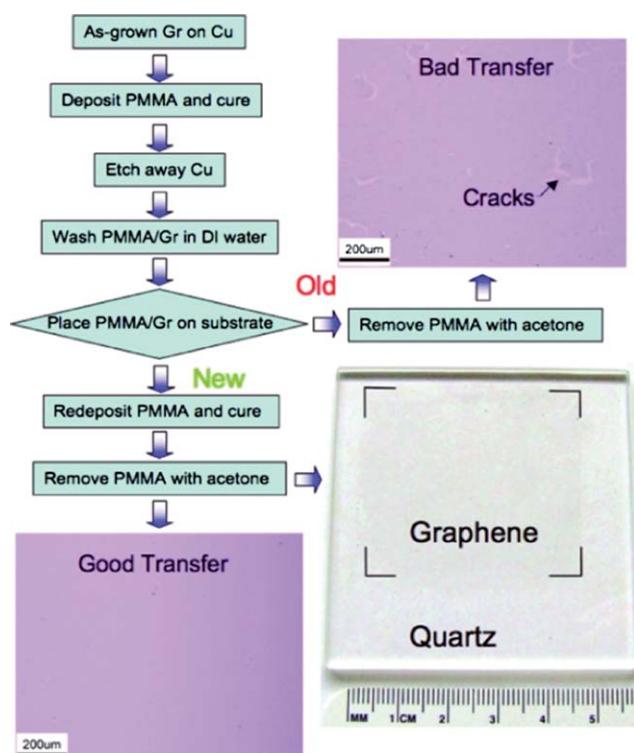


Fig. 8 Processes for transfer of CVD graphene films using a second layer of PMMA coating and curing. The top-right and bottom-left optical microscopy images show the morphology of graphene films transferred on SiO₂/Si wafer via "bad" and "good" transfer, respectively. Reproduced from ref. 35 with permission from the American Chemical Society Copyright 2009.

contact. Graphene transferred with the additional coating step showed improved quality, showing lower sheet resistance and high optical transmittance. Graphene contact on the substrate was further improved by heat treatment.⁸⁵ This method achieved graphene transfer with 98% coverage with only a few cracks and holes. In this way PMMA transfer became reliable enough to move graphene onto perforated substrates used for Raman spectroscopy and transmission electron microscopy (TEM) for studies of suspended graphene films.

Even with this improvement another problem surfaced. PMMA often was not fully washed away with acetone and remained as a residue. These residues tend to have a *p*-doping effect on graphene and cause carrier scattering. This can degrade the electrical and physical quality of graphene and decrease the carrier mobility.⁸⁶ Conventional semiconductor cleaning methods could wash off such polymeric contaminants but the process is too harsh for graphene. An alternate solution presented involved thermal annealing of graphene in a vacuum furnace under H₂-Ar or H₂-N₂ environment at 200–400 °C.^{87,88} Fig. 9a and b show the AFM images before and after thermal annealing at 300 °C for 3 hours in UHV. In the before-annealing image, the graphene surface is rough with PMMA residue; in the post-annealing image, the surface is smooth and even. The electrical results clearly indicated reduction in *p*-doping after the thermal treatment.

A useful transfer technique often carried out with PMMA support is "layer-by-layer" multiple stacking. Because it was

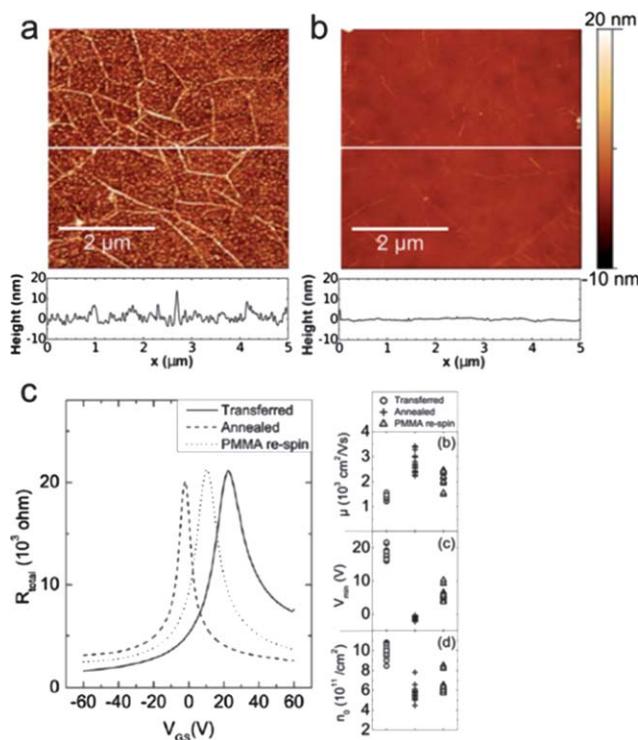


Fig. 9 Thermal annealing of graphene for removal of PMMA residues. (a and b) AFM images of graphene transferred onto SiO_2/Si substrate after acetone treatment (a) and after thermal annealing at $300\text{ }^\circ\text{C}$ for 3 hours under UHV condition (b). (c) CVD graphene based FET devices are measured by back gate after the annealing and PMMA re-spin process. Reproduced from ref. 86 with permission from the American Institute of Physics Copyright 2011.

reported that overall sheet resistance decreases with an increased number of layers, stacking three to four layers of graphene has been a common method for high quality device making. Originally for multiple stacking, PMMA coating, graphene transfer, and PMMA washing were repeated for each layer of graphene added.^{35,89,90} Therefore, if each layer has unwashed PMMA residue, as more layers are added more residue accumulates. This significantly reduces the carrier mobility and increases the sheet resistance of graphene, negating the purposes of graphene multiple stacking. In order to minimize PMMA use and damage to the quality, Wang *et al.* transferred the first PMMA/graphene layer freed from Cu onto a new graphene grown on Cu foil.¹⁶ Annealing these layers at $120\text{ }^\circ\text{C}$ for 10 minutes allows $\pi-\pi$ interactions to form between the two graphene layers. Etching the Cu leaves two graphene layers supported with single PMMA coating. Repeating these steps produces stacked graphene layers with only one PMMA coating and PMMA can be washed away only once when the desired numbers of layers are obtained. With the new stacking method, graphene layers showed improved sheet resistance compared to the original layer-by-layer transfer method.

Another interesting approach for graphene transfer using a PMMA coating is an electrochemical delamination process for CVD graphene on a Cu substrate, proposed by Wang *et al.*⁹¹ As in most other approaches, the PMMA layer acts as a supporting layer that prevents rolling or tearing of graphene during the

transfer process. In an electrolytic cell, an aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ is used as the electrolyte and PMMA/graphene/Cu and glassy carbon were used as the cathode and anode, respectively. Slight etching of Cu together with hydrogen gas bubbles emerging between graphene and Cu layer gently induces lift-off of the PMMA/graphene. Afterwards graphene can be transferred and PMMA is washed away as in a typical transfer. Because the process involves only a minuscule amount of Cu etching, it can be reused for graphene growth after the lift-off. The method also improves the quality of graphene due to the electrochemical polishing and thermal restructuring of the Cu foil.

Like the work of Yu *et al.* there are many efforts to completely avoid chemical etching of graphene metal substrates; however, because of their reliability and familiarity, PMMA and PDMS are still heavily used in graphene transfer. As the newly developed mechanical exfoliation of graphene still show limitations, cleaner removal of residues along with the search for gentler chemical etchants are continued to maintain high graphene quality. For laboratory scale graphene transfer, polymer supported transfer will most likely continue to be a popular method for a while.

3. Large-scale continuous transfer

Thermal release tape can be used as an alternative to the polymers mentioned above. For example, as shown by the works of Caldwell *et al.*, thermal release tape can be applied with a steel pressure plate on epitaxially grown graphene on SiC to aid the transfer.⁶⁵ By the force of the adhesive, the graphene is pulled from the SiC substrate. After placing the pulled graphene/tape on a desired substrate, simply applying heat releases the tape.

However, thermal release tape is not merely an alternative to polymers. The true merit of thermal release tape lies in its application for roll-to-roll transfer of graphene. Roll-to-roll is a process typically used in the paper or metal rolling industry where two rollers spin together while applying heat and pressure to the paper or metal in-between. The process is easily scalable and allows continuous production of the material of interest. While polymer supports are useful for wafer-size graphene transfer at best, thermal release tape support used in combination with roll-to-roll process has successfully supported the transfer of graphene with 30 inch diagonal dimension.²⁹ In this process, CVD graphene grown on rounded Cu foil inside an 8 inch diameter reactor is attached with thermal release tape and left in etchant for the removal of Cu. Afterwards it is transferred onto a flexible PET substrate and simply moved between two rollers with modest heating of $120\text{ }^\circ\text{C}$. The heat removes the adhesiveness of the tape and the released graphene adheres to the flexible substrate (Fig. 10a and b). The layer-by-layer stacking of graphene can also be accomplished with thermal release tape in similar manner to a PMMA support. A graphene device made by the roll-to-roll method on PET showed an effective hall mobility of $7350\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. Fig. 10c shows the application of roll-to-roll graphene on PET as a touch screen panel.

During the roll-to-roll process, there is a possibility that when the rolling speed is set too fast or when the transfer substrate is

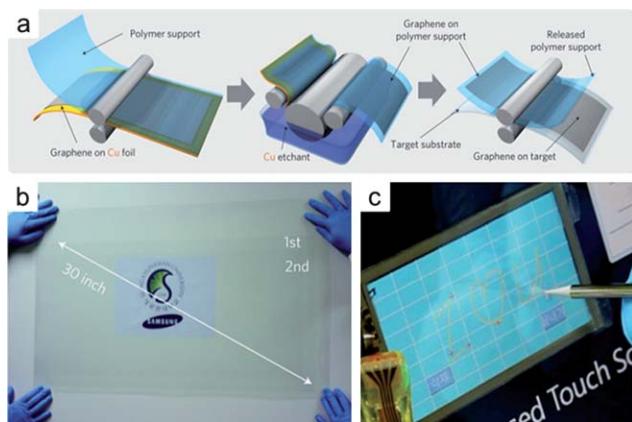


Fig. 10 Roll-to-roll production of large-scale, continuous graphene film on flexible substrate. (a) Schematics of the roll-based transfer procedure of graphene films. The process includes attachment of a polymer support on graphene/Cu foil, copper etching, and dry-transfer-printing on a target substrate. (b) A transparent and flexible graphene film with a large-scale area (30 inch). (c) Photograph image of first-fabrication of graphene-based touch panel. Reproduced from ref. 29 with permission from the Nature Publishing Group Copyright 2010.

rigid, shear stress causes damage to graphene layers, creating cracks or holes. In addition, just like PMMA, thermal release tape can leave residue.²⁹ In order to adapt large scale thermal release tape transfer for transfer on rigid substrates, the Hong group suggested using a hot pressing method instead of roll-to-roll.⁹² Instead of putting the tape/graphene/substrate through heated rollers, it is simply pressed by a large hot plate from the top and bottom of the tape/graphene/substrate. This eliminates the possibility of graphene ripping by shear stress and the method can be used flexibly for substrates of any thickness and size. With possible development of continuous synthesis of graphene in large scale, roll-to-roll transfer and hot pressing techniques are hoped to help develop industrial-size production of graphene in the near future. Fig. 11 shows a diagram of the hot pressing method and the resistance of the transferred graphene using the method.

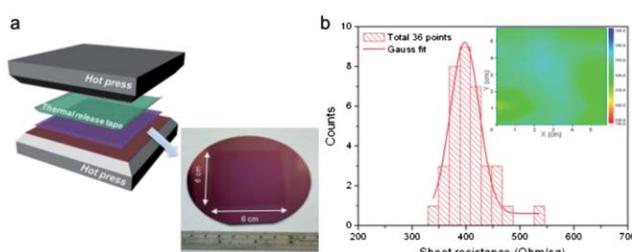


Fig. 11 Dry transfer of graphene films based on a hot-pressing method (a) A schematic illustration of hot pressing method for graphene and photo image of graphene film on SiO₂/Si wafer (b) Histogram of the sheet resistance of the graphene film on SiO₂/Si wafer transferred by hot pressing. The insert in (b) is a contour image corresponds to the spatial distribution of sheet resistance on the graphene film. Reproduced from ref. 92 with permission from the American Chemical Society Copyright 2012.

4. Transfer-free synthesis

Even with development and improvement of various transfer methods, the advantages of getting by without a transfer process drives researchers to develop transfer-free graphene growth techniques. As mentioned before, transfer introduces many steps in which graphene can be damaged. Polymers and thermal release tape can leave residues and all physical transferring stages are prone to ripping and tearing due to human error. With these unavoidable problems, development of transfer-free processes has become one of the most recent interests in this field. Several research groups have developed target substrate-specific methods for direct graphene growth.⁹³⁻⁹⁷ In order to avoid transfer steps, these groups have researched ways to grow graphene directly on the substrate that they would have transferred graphene to after the synthesis.

For device fabrication on SiO₂/Si substrates, Levendorf *et al.* reported direct graphene growth on 500 nm Cu (and a thin layer of Ni for adhesion) evaporated onto the substrate (Fig. 12).⁹³ Using a thinner Cu layer would expedite the etching but a layer thinner than 500 nm produced graphene of low quality. After the graphene is grown, a photoresist is applied to protect the areas to be made into devices. The rest are exposed to oxygen plasma and removed. With the photoresist still intact, the patterned graphene on the Cu/Ni metal and SiO₂/Si are put in a continuously refreshed etching chamber. This removes all of the exposed metals (and metals underneath a thin strip of graphene that is part of the device design), while leaving the islands of metals underneath the protected graphene layers. Finally the removal of the photoresist layer prepares the device for performance testing. Although the method still involves etching, the absence of a transfer step largely reduces possibility of tearing holes in the device and allows for large scale production of arrays of devices. The Raman study showed graphene of excellent quality with

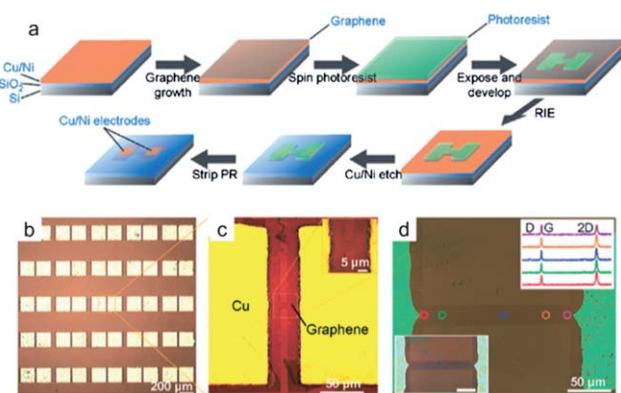


Fig. 12 Transfer-free fabrication of CVD graphene device arrays. (a) Schematic diagram of device fabrication processes with CVD graphene. (b) Large area view of fabricated graphene transistor arrays. (c) A single transistor image of the dashed box in (b) that shows clearly the fabricated graphene device around the edges of the Cu/Ni as well as the graphene channel. (d) An optical image of the fabricated graphene channel in the device. The inset of (d) shows the Raman spectroscopy on graphene channel; the quality of graphene is estimated from the intensity, shape, and position of the D-, G-, and 2D-peaks. Reproduced from ref. 93 with permission from the American Chemical Society Copyright 2009.

universally low D peaks as shown in Fig. 12d. The device showed good electron mobility of about $700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Ismach *et al.* also grew graphene directly on Cu-deposited insulating substrates (Fig. 13a).⁹⁴ What differentiates their method is that instead of etching Cu after the synthesis, they kept the graphene/Cu/insulating substrate from 15 minutes to 7 hours in high temperatures and conducted controlled dewetting and evaporation of the Cu layer. The study showed that it takes more than 6 hours for the Cu layer to completely evaporate; however, after 2 hours of the high temperature reaction, the graphene quality starts to deteriorate. The Raman peak showed that after 6 hours, the D peak of graphene is significantly larger than that of graphene kept in the reactor for fewer hours. Although the method completely avoids metal etching and transferring, the complete removal of Cu comes at the cost of long reaction time and degradation of graphene quality.

Another group showed a quite different approach for growing graphene on SiO_2/Si substrates. Su *et al.* closely studied the mechanism of graphene growth on Cu and conjectured that carbon atoms can travel through Cu grain boundaries during CVD synthesis (Fig. 13b).⁹⁵ Therefore, when graphene is grown on Cu deposited onto SiO_2/Si substrates, diffused carbon atoms can form a graphene layer underneath the deposited Cu. This synthesis approach does eliminate the transfer steps, but the Cu layer is peeled off with tape or etched away using common Cu etchants. The mechanical force tears the graphene along random crack lines and makes it impossible to control the size and quality of the remaining graphene on the SiO_2/Si substrate. When a small area of graphene is required, this method is capable of providing it without lengthy transfer and etching process, but for producing high quality, large area graphene, it requires etching.

Similarly, work by Shin *et al.* synthesized graphene underneath the metal layer.⁹⁶ In this work, a layer of carbon source containing self-assembled materials (SAM), such as PMMA, polystyrene, and polyacrylonitrile, was sandwiched between a SiO_2/Si wafer and a metal layer. The sandwich structure was subjected to

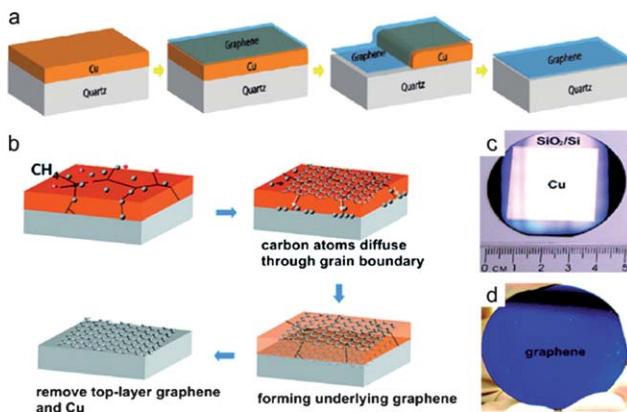


Fig. 13 Schematics of the direct chemical vapor deposition of graphene film on the target substrate using metal evaporation (a) and carbon diffusion through Cu grain boundaries (b). (c and d) Photo images before (c) and after (d) Cu etching, showing the graphene grown between Cu layer and SiO_2/Si wafer. Reproduced from ref. 94 and 95 with permission from the American Chemical Society Copyright 2010, 2011.

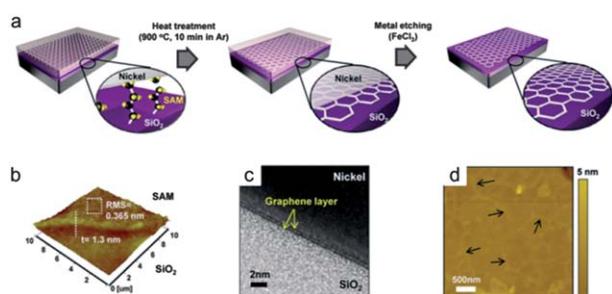


Fig. 14 Transfer-free growth of few layer graphene films by a solid carbon source. (a) Schematic illustration of graphene growth procedures using self-assembled monolayers. (b) AFM image of SAM deposited on SiO_2/Si substrate. The thickness of SAM layer is measured by tapping mode. (c) High resolution-TEM image of the graphene films between Ni layer and SiO_2/Si substrate. (d) AFM image of the surface of graphene films on SiO_2/Si substrate after Ni etching. Reproduced from ref. 98 with permission from WILEY-VCH Verlag GmbH & Co. KGaA Copyright 2011.

a high temperature pyrolysis reaction in which the SAM materials convert to a graphene layer directly on SiO_2/Si wafer.⁹⁶ Fig. 14a illustrates the process of the SAM material converting to graphene layers. With this method, high quality graphene with carrier mobility of $\sim 4400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron density of $2 \times 10^{12} \text{ cm}^{-2}$ was synthesized. The fact that the graphene layer forms between the metal and the wafer seems to reduce wrinkles and ripples that typically form when the graphene is grown on top of the metal. The method doesn't remove the etching process but it certainly makes the etching process easier since the metal layer is exposed on the top. After the metal etching, graphene is ready for characteristic study or further device making without additional steps.

There also has been a direct synthesis developed for flexible plastic substrate. While many rigid insulating substrates like SiO_2/Si wafer, quartz and sapphire can endure high temperature CVD synthesis, most flexible substrates are not suitable for graphene growth because of their low melting points. In order to make flexible graphene devices, then transferring graphene onto flexible substrates seems inevitable. However, Kim *et al.* utilized inductively coupled plasma-CVD (ICP-CVD) to synthesize graphene directly on PI deposited with pre-patterned Cu at low temperature.⁹⁹ After the ICP-CVD synthesis with temperatures below 300 °C, the Cu metal is etched away. Interestingly, the etching process does not require extra polymer support. As Cu is slowly etched away, graphene and PI establishes $\pi-\pi$ interactions and van der Waals forces and stick to each other. Even without the support, graphene stayed intact in good condition. The schematic of the fabrication procedures are shown in Fig. 15. In a sense, there is indeed a transferring stage but since it occurs simultaneously with Cu etching, a conventional polymer supported transfer is avoided. Nevertheless, although there is no transfer-induced damage, low temperature growth produces graphene with relatively low quality. The Raman D peak of the measured graphene was high in intensity and sheet resistance values ranged from 400 to 8000 Ohms for graphene grown 30 to 180 seconds duration. Such quality would not be sufficient for making graphene electrode devices, but it is ample to fabricate a well-functioning strain gauge sensor.

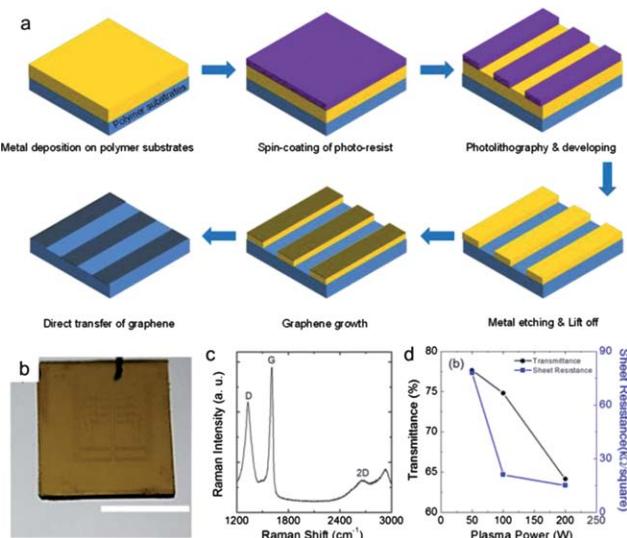


Fig. 15 Direct growth of graphene on Cu/PI substrate at low temperature (a) Schematic diagrams of direct synthesis of graphene on PI substrate using ICP-CVD (b) Photo image of the pre-patterned graphene film transferred onto a PI substrate (c) Raman spectrum of graphene grown on Cu/PI substrate (d) Electrical and optical properties of graphene films as a function of plasma power. Reproduced from ref. 99 with permission from Institute of Physics, Copyright 2012.

Conclusions

From mechanical exfoliation to polymer supported transfer to transfer-free techniques, a myriad of ways to deliver graphene to the desired substrates have evolved. While each technique differs in its details, all of them try to address the common problems of transfer of large area graphene: reducing physical damage, and minimizing the disturbance of electrical properties from substances used during the transfer. So far, there seems to be no clear winner for best transfer technique. Mechanical exfoliation avoids etchants and polymers but induces physical damage; polymer supports leaves residues; transfer-free techniques are substrate or application specific and difficult to widely adapt. In order for graphene production to evolve into the industrial scale, continued improvement of scalable transfer methods is required in conjunction with reliable, large-scale synthesis.

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