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Advances in transferring chemical vapour deposition graphene: a review

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The unique two-dimensional structure and outstanding electronic, thermal, and mechanical properties of graphene have attracted the interest of scientists and engineers from various fields. The first step in translating the excellent properties of graphene into practical applications is the preparation of large area, continuous graphene films. Chemical vapour deposition (CVD) graphene has received increasing attention because it provides access to large-area, uniform, and continuous films of high quality. However, current CVD synthetic techniques utilize metal substrates (Cu or Ni) to catalyse the growth of graphene and post-growth transfer of the graphene film to a substrate of interest is critical for most applications such as electronics, photonics, and spintronics. Here we discuss recent advances in the transfer of as-grown CVD graphene to target substrates. The methods that afford CVD graphene on a target substrate are summarized under three categories: transfer with a support layer, transfer without a support layer, and direct growth on target substrates. At present the first two groups dominate the field and research efforts are directed towards refining the choice of the support layer. The support layer plays a vital role in the transfer process because it has direct contact with the atomically thin graphene surface, affecting its properties and determining the quality of the transferred graphene.

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1. Introduction

Graphene, arguably one of the most attractive carbon materials of the 21st century, continues to receive a great deal of attention.[1] Both academia and industry have explored the outstanding properties of graphene in search of advanced structures, engineered architectures, and novel devices that can revolutionize the

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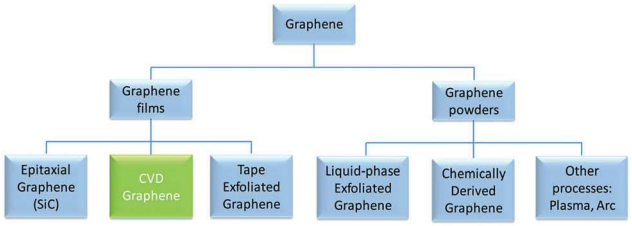

Fig. 1 Forms of graphene.

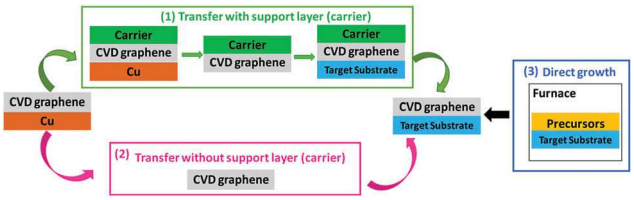

Fig. 2 Schematic of various routes to obtain CVD graphene on target substrates.

technology. The possibility for building integrated circuits on a graphene wafer[2,3] together with promising applications in flexible electronics,[4] transparent electrodes,[5] water desalination,[6] and energy storage[7–9] have motivated extensive studies on the synthesis,[10] transfer,[5,11–14] chemical modification,[15–19] and characterization of graphene films.[20–23]

Based on the morphology, graphene can be categorized into two groups: graphene films and graphene powders (Fig. 1). Although graphene powders can be produced in large quantities and dispersed in solvents for both solution-based and film-based applications,[19] this form of graphene is not particularly suitable for electronic applications that rely on the planar 2-D properties of graphene. Graphene powders find a broad range of practical applications in energy storage[7–9] and thermal management.[24] Graphene films can be divided into epitaxial graphene on SiC, chemical vapour deposition (CVD) graphene (mainly on Cu, Ni), and scotch tape exfoliated graphene on various substrates.

Wafer scale single domain graphene is required to build uniform graphene integrated circuits (IC) in a fashion compatible with the current industrial fabrication facilities. Centimeter-scale single-crystalline growth of CVD graphene has been successfully demonstrated,[25–28] which makes this form of graphene an appealing candidate for graphene IC, flexible electronics, and spintronics. Currently, large domain CVD graphene films are synthesized on metal catalyst substrates, such as Cu or Ni films, and therefore a subsequent transfer step to a substrate of interest is required for electronic applications.

Methods for the preparation of CVD graphene films on substrates of interest can be classified into three main categories as shown in Fig. 2: (1) transfer with the help of a support layer onto target substrates; (2) transfer without any support layer onto target substrates; and (3) direct growth of CVD graphene on target substrates without any post-growth transfer process. Below we review the recently developed graphene transfer methods from the perspectives of mechanism, cleanness, quality (defects, cracks and folds), reliability, and cost.

2. CVD graphene transfer methods

A graphene transfer technique has to solve two problems: (1) the separation of the graphene layer from the metal substrate (Cu/Ni) and (2) the protection of the graphene integrity after the separation.

2.1 Graphene transfer with a support layer

A conventional and very efficient way to protect graphene from external forces during the transfer process is the use of a support layer coated on top of the graphene surface. As metal substrates can be easily removed by etching solutions or peeled

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off after special pre-treatment (such as intercalation of gas bubbles or self-assembled monolayers – discussed below), the main factor that determines the quality of the transferred graphene is the support layer. A good support layer should possess the following characteristics in order to minimize the degradation of graphene's quality during the transfer process: (a) to be flexible, (b) to provide sufficient mechanical support to the graphene films, and (c) to be easily removed from the graphene surface at the end of the process.

2.1.1 Polymer-based graphene transfer. Polymers are the most widely used support layers in current graphene transfer methods. A carrier polymer should form a flexible thin film to assure conformal contact with graphene and the target substrate, and be mechanically strong to provide sufficient support to the graphene layer. The surface energy of the polymer carrier and the target substrate plays a critical role in the quality of the transferred graphene in terms of residues, cracks, and folds.[29–31] The adhesion force between elastic solids is proportional to the surface energy according to the modified Hertz theory.[32] The lower the surface energy of the polymer carrier, the weaker the adhesion force with the graphene surface, and thus the easier it will be to remove the polymer by mechanical forces or dissolution, leaving fewer residues. On the other hand, the target substrate should have high enough surface energy to assure low contact angle of the liquid trapped between the substrate and graphene to achieve a conformal contact between graphene and the substrate, which will reduce the number of cracks and folds in the transferred graphene. The surface energy of substrates can be enhanced by multiple techniques, such as oxygen plasma treatment and acid etching.[33,34]

Another important fact is that graphene has a negative thermal expansion coefficient while most polymers have a positive one,[35,36] thus using a polymer support layer is very likely to introduce strain or cracks in graphene.

Poly(methyl methacrylate), PMMA-assisted graphene transfer. The early-stage CVD graphene transfer methods adopt poly(methyl methacrylate) (PMMA) as the support layer.[11,37] Typical steps that comprise this group of methods are illustrated in Fig. 3. The process begins with coating one side of the as-grown CVD graphene on a copper foil with a PMMA solution in anisole or chlorobenzene.[11,37] Note that in a typical CVD process graphene grows on both sides of the Cu foil. The PMMA is then polymerized and the graphene on the other side of Cu is removed by O_2 plasma etching. In the next step of the process, the sample is placed on the surface of an etching solution, for example $FeCl_3$ solution, to dissolve the copper. Finally, the etching solution is replaced with clean water multiple times. The PMMA/graphene film is lifted off with a target substrate and placed on a hot plate for high-temperature baking to remove water residues trapped between

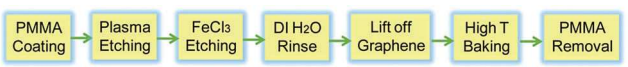

Fig. 3 Schematic illustration of conventional PMMA-assisted graphene transfer processes.

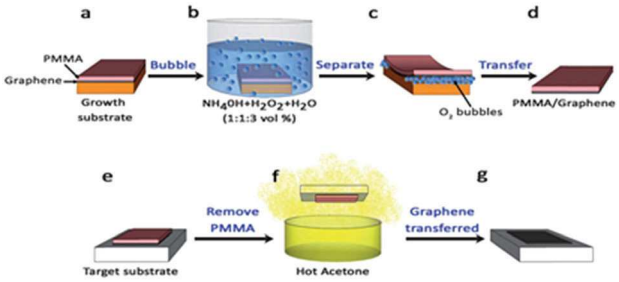

Fig. 4 Schematic of the bubbling route for transfer of graphene on arbitrary substrates. (a) Deposition of a PMMA support/carrier layer on graphene. (b) Transfer of the substrate into an $NH_4OH + H_2O_2 + H_2O$ (1 : 1 : 3 vol%) bath in which bubbling due to the release of O_2 gas occurs. (c) Intercalation of the O_2 gas bubbles at the graphene–substrate interface leading to (d) gradual detachment of the PMMA–graphene film. (e) Transfer of the separated graphene film onto the target substrate and (f) removal of PMMA using hot acetone vapour. (g) Graphene is successfully transferred onto an arbitrary substrate. Reproduced with permission from ref. 39. Copyright 2014 The Royal Society of Chemistry.

the graphene and the target substrate and improve the contact between them.

The demand for large scale, low cost, efficient transfer of clean CVD graphene to arbitrary substrates, has led to the development of various optimized and upgraded PMMA transfer techniques. For example, Kim *et al.* made use of low average molecular weight PMMA to obtain cleaner graphene;[38] Gorantla *et al.* intercalated oxygen bubbles into the graphene–substrate interface, and then peeled off the PMMA–graphene film without dissolving the metal substrate (Fig. 4).[39] This bubbling method strategically made use of the O_2 bubbles to weaken the adhesion between the graphene layer and metal substrate, and thus successfully separated the graphene without the need to dissolve the metal, which lowers the cost as the growth substrates can be reused. A similar mechanism was previously reported which utilizes electrochemical processes to generate the bubbles;[40] in this approach the PMMA/graphene/Pt was immersed in a solution of NaOH, and the H_2 bubbles generated at the interface of the graphene/Pt facilitated the delamination of the PMMA/graphene from the Pt substrate.

Another example of separation of graphene from the growth substrate by weakening the interaction between them is the intercalation of alkanethiol self-assembled molecules (SAMs) into the graphene–metal interface by immersing the PMMA-coated CVD graphene into a solution of 1-octanethiol in ethanol (Fig. 5). The formation of SAMs helps in releasing the compressive strain of graphene and weakens the interaction between graphene and the metal substrate.[41] This method is effective in transferring graphene to water-sensitive substrates as no water is introduced during the transfer process. After the separation from the growth substrate, the PMMA/graphene film is placed on top of the target substrate, and subjected to high-temperature baking to improve the contact between graphene and the substrate.[37] Although the baking process reduces the folding and cracks in graphene, it does not fully eliminate them as the surface energy of the target substrate also plays an important role in the flatness of the transferred graphene.[31,39]

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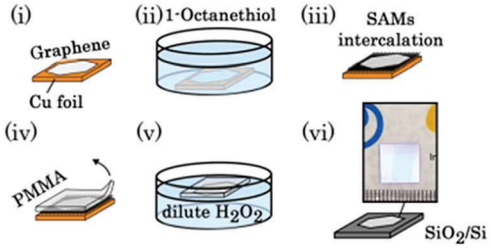

Fig. 5 Schematic of the thiol-intercalation graphene transfer method. (i–iii) Intercalation of octanethiol molecules. (iv) PMMA was spin-coated on graphene and baked at 110 °C. Cu foil was then mechanically delaminated while the PMMA layer was supported by thermal release tape. (v) PMMA/graphene films were floated on the diluted H_2O_2 solution to remove the residual thiol molecules. (vi) An optical image of the graphene on 285 nm SiO_2/Si transferred from Cu foil using the thiol-intercalation method. Reproduced with permission from ref. 41. Copyright 2016 The Royal Society of Chemistry.

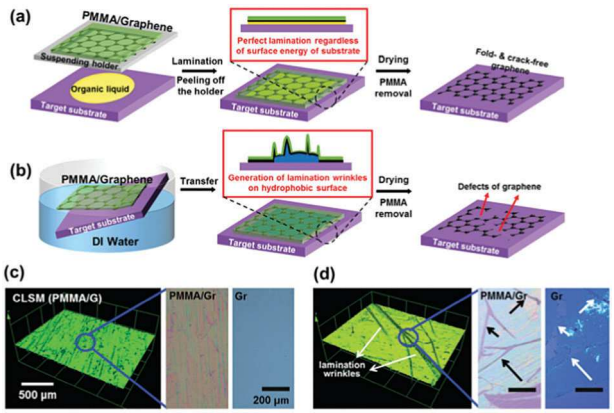

Fig. 6 Schematic diagram showing the graphene transfer steps in (a) the organic liquid transfer or (b) conventional wet transfer methods. Confocal laser scanning microscopy (CLSM) and optical microscope images of a PMMA/graphene film and of the final graphene layer obtained by (c) organic liquid transfer, or by (d) conventional wet transfer methods. Reproduced with permission from ref. 31. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

To improve the flatness of the transferred graphene, a wetting-assisted crack- and wrinkle-free graphene transfer method was proposed by wetting the target substrate with low surface tension volatile liquid droplets, such as heptane, before the PMMA/graphene film is placed on the target substrate (Fig. 6a).[31] The wrinkles and cracks present in the graphene samples obtained with the conventional PMMA wet transfer method (Fig. 6b and d) are largely reduced in the organic liquid (OL) transfer method, which is further confirmed by confocal laser scanning microscopy (CLSM) and optical microscopy (OM) as illustrated in Fig. 6a and c.

Instead of using bubbles to separate graphene and the growth substrate, Gao *et al.* introduced a face-to-face (F2F) transfer technique which takes advantage of the capillary bridges formed between the graphene film and the underlying substrate during etching of the metal catalyst.[13] In this method, both the growth and transfer steps are accomplished on a single wafer (Fig. 7).

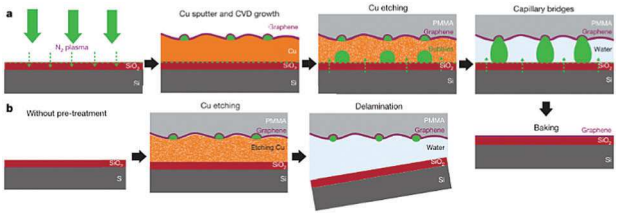

Fig. 7 Illustration of the face-to-face method for transferring graphene mediated by capillary bridges. (a) Schematic illustration showing "bubble seeding" by plasma treatment, CVD growth, Cu film etching, formation of capillary bridges and removal of water and PMMA. (b) Schematic illustration showing that in the absence of plasma treatment, delamination of the film results. Reproduced with permission from ref. 13. Copyright 2014 Nature Publishing Group.

The process begins with a plasma nitridation pre-treatment of the SiO_2/Si wafer, followed by the sputtering of Cu (700 nm) onto the surface of the SiO_2/Si wafer and the CVD growth of graphene. The wafer is then coated with PMMA and the layered structure PMMA/graphene/Cu/SiO_2/Si is immersed into an etching solution to remove Cu. The nitridation pre-treatment of SiO_2/Si is a critical step in this process because it generates silicon oxynitride on the silicon wafer that decomposes during the CVD growth and forms bubbles during the Cu etching, which are essential for the formation of capillary bridges between the graphene and the underlying substrate. Finally, PMMA is removed and the sample is baked to completely evaporate the infiltrated water. The F2F method avoids manual manipulation of the graphene and minimizes movement of the as-grown graphene, which results in crack-free wafer-scale graphene films on SiO_2/Si or quartz substrates. This method is applicable to stiff substrates with high melting points.

Although the quality of graphene has significantly improved due to optimization and upgrades, ultraclean transferred graphene is difficult to obtain as long as PMMA is adopted as the support layer. PMMA meets the first two requirements for an efficient graphene carrier: (a) it is flexible, which assures good contact between the graphene and the target substrate upon high-temperature baking and (b) it is sufficiently strong to protect the graphene from fragmentation by the surface tension of the etching solution. However, PMMA can hardly satisfy the third criterion as a support layer: (c) easy to remove from the graphene after transfer. It is well known that PMMA inevitably leaves residues on the surface of the graphene, which affect the electronic properties of graphene.[42,43] Despite the development of various post-transfer procedures to reduce the PMMA residues, such as high-temperature annealing in a mixture of H_2/Ar,[43] laser treatment,[44] and electrolyte cleaning,[45] current processes cannot fully remove the PMMA residues without introducing defects in the graphene film.

PDMS-assisted graphene transfer. Polydimethylsiloxane (PDMS) has been extensively studied and widely used in soft lithography, because it provides a cost-effective way to fabricate micro- and nanoscale devices.[46,47] In the original PDMS-assisted transfer method, multilayer CVD graphene is attached

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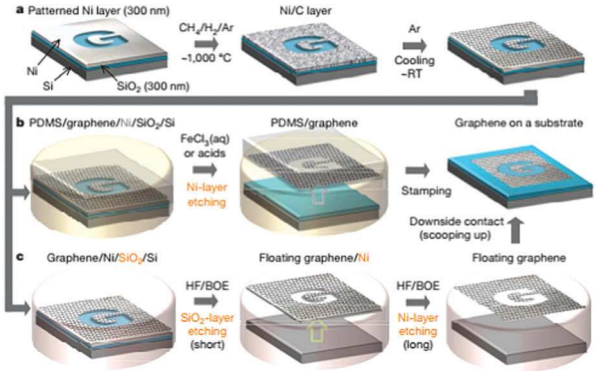

Fig. 8 Schematic of the PDMS-assisted graphene transfer for large-scale and patterned graphene films. (a) Synthesis of patterned graphene films on thin nickel layers. (b) Etching using $FeCl_3$ (or acids) and transfer of graphene films using a PDMS stamp. (c) Etching using buffered oxide etchant or hydrogen fluoride (HF) solution and transfer of graphene films at room temperature. Reproduced with permission from ref. 48. Copyright 2009 Nature Publishing Group.

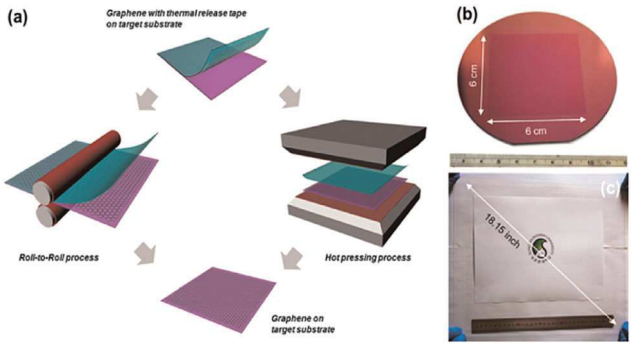

Fig. 9 (a) Schematic illustration of graphene transfer by R2R and hot pressing methods. (b) Photograph of a graphene film (6×6 cm^2) transferred onto an SiO_2/Si wafer by hot pressing. (c) Photograph of an 18-inch graphene film transferred on a glass substrate by hot pressing. Reproduced with permission from ref. 52. Copyright 2012 American Chemical Society.

to a crosslinked solid PDMS elastomer, and transferred to target substrates by a simple "stamping" process after Ni is etched away[48] (Fig. 8). Despite the large-scale conformal contact between the PDMS elastomer and target substrates, uniformly strong adhesion between the entire graphene surface and the target substrate is necessary theoretically for intact graphene transfer. Therefore, this method has high requirements for the cleanliness, flatness, and rigidness of the target substrate and it often produces fragmental graphene flakes experimentally.[12] In fact, in most cases PDMS functions as a rigid holder for the realization of dry transfer of graphene rather than as a support layer.[12,49] However, PDMS-assisted methods have inherent drawbacks, such as the introduction of adhesive residues and defects in the transferred graphene films,[37,50] which deteriorate the excellent electronic properties of graphene and restrict their applications in commercial devices.

Thermal release tape-assisted graphene transfer. Thermal release tape (TRT) is a tape with specific adhesives which strongly adheres to substrates at room temperature while losing adhesion at high temperature (above ~100 °C). A representative thermal release tape-assisted graphene transfer method is the roll-to-roll (R2R) technique.[5,52] This method inherits the large-scale and high-throughput characteristics of roll-to-roll production.[53,54] Although the R2R graphene transfer method is efficient in transferring large area graphene to flexible substrates (Fig. 9a) for the fabrication of graphene flexible electronics, it is not suitable for transferring graphene to rigid substrates such as wafers and glass. Kang *et al.* reported a hot pressing method using two metal plates to press TRT/graphene onto rigid substrates mediated by precise temperature and pressure after Cu is etched away (Fig. 9a).[52] Thus, it is widely accepted that the thermal release tape-based graphene transfer methods (R2R and hot pressing) can achieve the large-scale transfer of graphene on both flexible and rigid substrates. The target substrates are not exposed to water during the transfer processes, which defines R2R and hot pressing as dry transfer methods and makes them suitable for transferring graphene onto water-sensitive substrates.[55]

It is worthwhile to mention that although a pressure-sensitive tape can also be utilized to transfer graphene to various substrates (in this case the release is mediated by pressure instead of heat),[30] the adhesive residue remains an unresolved issue.[51]

Natural polymer-assisted graphene transfer. Green chemistry aims at the use of renewable materials and biomass is the major source of renewable feedstock.[56] Use of renewable feedstock for graphene transfer will reduce the production cost and the generated waste for industrial large-scale production of graphene devices in the long run. The selection of natural polymers for graphene transfer is based on three requirements as discussed earlier: (a) ability to form flexible films or stamps; (b) ability to provide sufficient mechanical support to the graphene film; and (c) ease of removal from the graphene surface. Recent advances in the development of clean, cheap, and efficient graphene transfer methods were made by use of natural polymers (derivatives) as the support layer – such as cellulose acetate[14] derived from cellulose and agarose[57] extracted from seaweed. Because the support layer accounts for a large portion of the expenses in the graphene transfer process, the overall cost of the transfer is significantly reduced by replacing PMMA with natural polymers such as cellulose acetate or agarose.

Cellulose acetate film serves as an effective carrier for graphene transfer. This natural polymer forms a soft flexible thin film on top of graphene, protecting it from unfavorable forces and contaminations during the transfer process. This method produces high quality, clean graphene films as confirmed by Raman spectroscopy; Fig. 10b shows that the Raman spectrum of transferred single layer graphene (SLG) has nearly no D peak. Reducing the defect and residue levels in graphene is expected to also improve the performance of the fabricated graphene devices. For example, the on-off ratio of the transferred graphene is enhanced by ~60% when the cellulose acetate assisted method is used for graphene transfer as compared to the PMMA-assisted transfer (Fig. 10c).[14]

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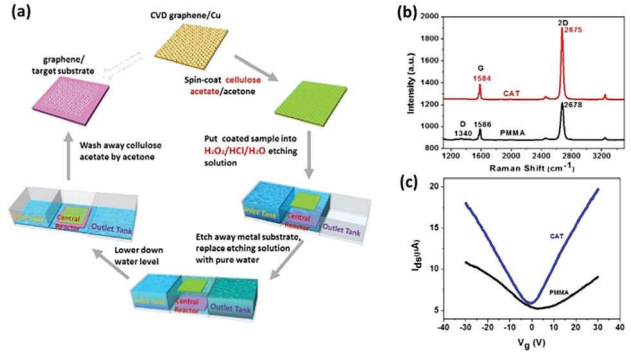

Fig. 10 (a) Schematic illustration of the cellulose acetate-assisted transfer (CAT) of graphene. (b) Raman spectra of single layer CVD graphene transferred by the CAT and PMMA methods. (bed). (c) Drain–source current *vs.* gate voltage of the graphene field-effect-transistor devices. Reproduced with permission from ref. 14. Copyright 2016 Elsevier.

Although natural polymers can produce cleaner and higher quality graphene than PMMA and PDMS-assisted techniques, the complete removal of the adsorbed polymer requires tedious cleaning processes, which is a built-in problem for the polymer-supported graphene transfer methods. Thus, novel non-polymer carriers are highly desired for reliable ultraclean graphene transfer.

2.1.2 Non-polymer based graphene transfer

Metal-assisted graphene transfer. In a typical metal-assisted graphene transfer technique, first a thin layer of metal is deposited on top of the as-grown graphene, followed by etching of the growth substrate – Cu or Ni. After placing the graphene on the target substrate, the deposited metal is dissolved in acids or an etching solution (Fig. 11).[58,59] The deposition of metals is most often accomplished by e-beam evaporation, which offers a precise deposition of metal thin films with controlled thickness, high purity, uniformity, and cleanliness. In addition, e-beam evaporation is a mild process as compared to other deposition methods, such as sputtering that generates a plasma of charged particles with high energy, therefore introducing defects and even severely damaging the graphene layer.[60]

Despite the complete removal of the metal, this method is not suitable for commercial application due to the complicated procedures and high cost associated with e-beam evaporation of transition or precious metals. Furthermore, in the last step, which is the removal of the deposited metals, the graphene layer is exposed to a harsh etchant, which may dope graphene[54] or introduce defects.[55]

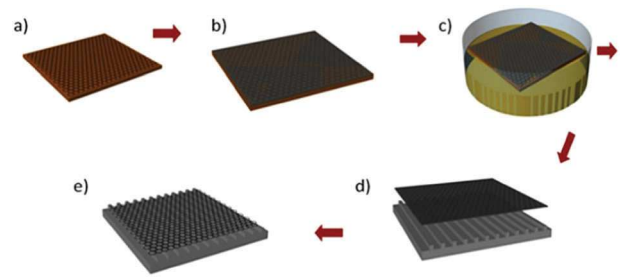

Fig. 11 Scheme of a metal-assisted graphene transfer. (a) CVD graphene on Cu foil; (b) e-beam evaporation of 15 nm of a Ti layer; (c) wet etching of Cu; (d) Gr/Ti transfer onto an Si substrate; (e) graphene on the Si substrate after Ti etching. Reproduced with permission from ref. 58. Copyright 2016 Elsevier.

The direct use of the growth substrates, *i.e.* Cu or Ni, as the support layer will simplify the procedures and reduce the cost. However, most Cu or Ni films used for CVD graphene synthesis are very thick ($\sim$25 μm)[10,37,61] and therefore not as flexible as polymer thin films. If the metal foil thickness can be reduced – for example by chemical etching, atomic layer etching, or laser ablation, the growth substrate can serve as a support layer. This approach for graphene transfer has not been reported to the best of our knowledge.

It is worth mentioning that with the help of organosilane SAMs, direct transfer of the as-grown CVD graphene to target substrates has been realized without the removal of the SAM layer.[51]

In summary, current metal-assisted graphene transfer methods are not suitable for cost-effective, high quality, ultraclean graphene-based electronic applications.[14]

Small molecules assisted graphene transfer. The dissolution of polymers is a complex process, which is affected by many factors such as cohesive density, heat of mixing, dipole interaction, and molecular weight.[62] Polymers do not dissolve instantaneously, and the dissolution mechanism involves separation of the polymer chains or diffusion of the chains through the polymer–solvent interface.[63] Thus, in most cases polymers leave residues on the surface of graphene. Replacement of polymers with small molecules adds a new route to graphene transfer. An ideal small molecule carrier should have good casting properties and the adhesion to the graphene surface should rely on van der Waals forces, avoiding covalent and ionic interactions. The small molecule carrier should be easy to remove from the graphene under mild conditions – either by dissolution or through a phase change (melting, sublimation). Sublimation at room or moderate temperatures is an attractive approach to remove the support layer from the graphene surface, because it can be applied to virtually any substrate of interest. Thus, the use of naphthalene, a small polyaromatic hydrocarbon, was demonstrated to produce ultraclean graphene films.[64] Melted naphthalene is drop-casted onto the surface of the CVD-grown graphene, and after dissolving the copper foil, the naphthalene-supported graphene is placed onto the target substrate and the naphthalene is sublimed in air (or vacuum), leaving a clean graphene film, as illustrated in Fig. 12. The naphthalene-assisted transfer (NAT) method is particularly useful where ultraclean graphene is needed, such as the chemical functionalization of graphene,[19,65,66] or where the target substrates are incompatible with organic solvents and high-temperature treatments.[64] Nevertheless, the naphthalene film is not as flexible as polymers, which impedes the formation of a conformal contact between graphene and large rigid substrates, therefore, posing a challenge for the integrity and continuity of graphene on the macro-scale.

Hexane-assisted graphene transfer. Instead of using solid thin films, liquid phase organic solvents can also be utilized as

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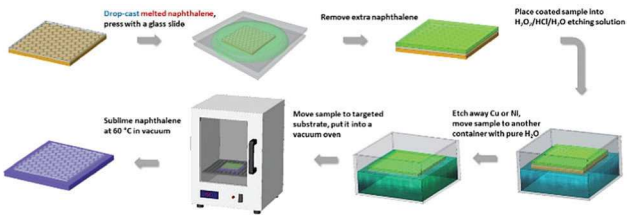

Fig. 12 Schematic illustration of the naphthalene assisted transfer of graphene. Reproduced with permission from ref. 64. Copyright 2017 IOP Publishing Ltd.

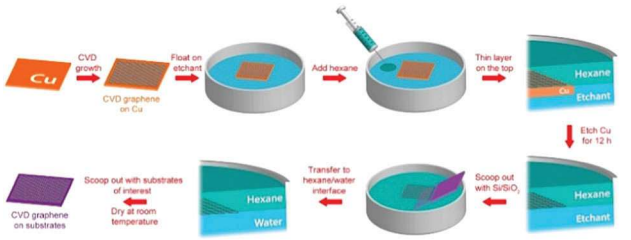

Fig. 13 Schematic of the polymer-free biphasic method for CVD graphene transfer. Reproduced with permission from ref. 67. Copyright 2016 American Chemical Society.

support layers as demonstrated by Zhang *et al.*[67] In a polymer-free biphasic method shown in Fig. 13, the authors use hexane, which has a function similar to the polymers, to stabilize and protect the graphene from the etching solution. A key advantage of the biphasic method is the extreme flexibility of the liquid hexane and therefore the organic layer makes good contact with the entire graphene surface and can conform to even coarse 3D structures.[67] Replacing polymers with hexane affords residue-free graphene that can be transferred to arbitrary substrates. However, because this wet method requires the use of target substrates to lift off the suspended graphene, it is not suitable for water-sensitive or hexane-soluble substrates.

Static charge based graphene transfer. In this clean lifting transfer (CLT) method, the as-grown graphene is attracted to the target substrate by electrostatic force, as shown in Fig. 14.[68]

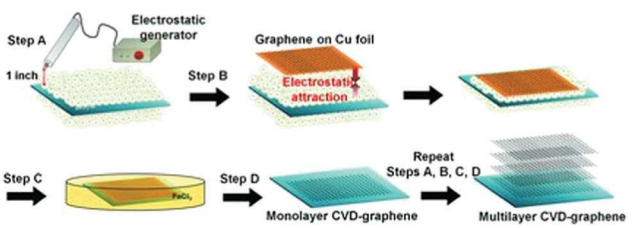

Fig. 14 Schematic illustrations of the CLT processes of transferring as-grown graphene on Cu foil onto a substrate. Step A: Accumulated charges were generated on the surface of the target substrate by an electrostatic generator. Step B: Cu/graphene was pressed onto the target substrate. Step C: Cu foil was etched away by iron nitrate etching solution. Step D: Graphene/target substrate was rinsed with deionized water and dried by N_2. Reproduced with permission from ref. 68. Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The CLT technique gives residue-free graphene because it makes use of static charges that act as a support layer. Without using any tangible carriers the method makes possible the transfer of large area graphene films on various substrates. Still, many folds are introduced in the transferred graphene, which inevitably affects the quality of the transferred graphene.[31,37,69]

2.2 Graphene transfer without a supporting layer

It is widely known that the surface tension of the etching solution, used to remove the growth substrate, could tear apart the graphene layer. That is why a support layer was proposed in the first place to protect graphene during the metal etching process.[11,14,31,37,48,58,59,64] An alternative approach to protect the graphene is the modification of the surface tension of the etching solution to a harmless level.[61] Lin *et al.* mixed isopropyl

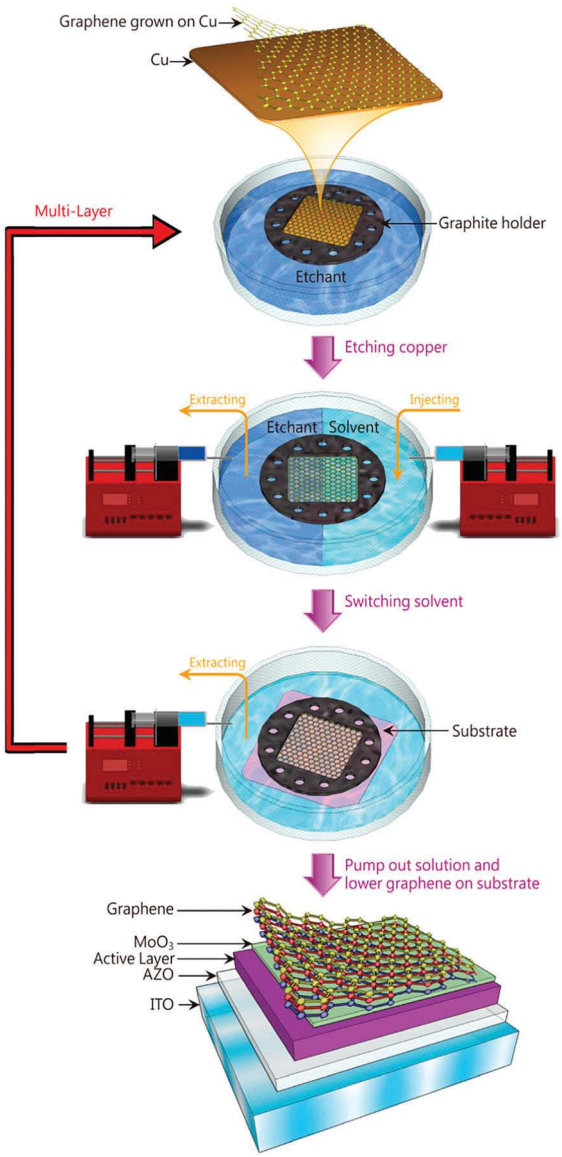

Fig. 15 Schematic illustration of the support-free graphene transfer process. Reproduced with permission from ref. 61. Copyright 2014 American Chemical Society.

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alcohol (IPA) with 0.1 M ammonium persulfate (volume ratio of 1 : 10) in order to reduce the surface tension of the etching solution.[61] As shown in Fig. 15, graphene on Cu was directly placed on the surface of the mixed etching solution confined by a graphite holder. After the Cu foil was completely dissolved, the mixed etchant was replaced with a fresh mixture of water and IPA by pumping out the etchant on one side and pumping in a fresh mixture on the other side of the bath. Finally, the graphene floating on the surface was lowered to the target substrate by slowly pulling out the remaining solution with a syringe pump. This support-free method successfully avoided contamination from the polymer and organic residues, and thus largely improved the quality of the transferred graphene. It should be noted, however, that due to the lack of support after Cu is etched away, the graphene can be easily cracked by solution fluctuations and other external forces, and thus the reliability and yield of this graphene transfer method remains a challenging task.

2.3 Direct growth of graphene without transfer

The defects introduced during detachment of the graphene from the growth substrate combined with imperfect adhesion of the transferred graphene to the target substrate inevitably impair the quality of the transferred graphene regardless of the transfer method. Therefore, an ideal way to obtain high-quality graphene is the direct growth on the substrate of interest. For example, direct growth of large area continuous graphene on insulating substrates is a promising direction in achieving high-quality graphene, as it avoids the tedious transfer processes that may degrade the quality of graphene.[70]

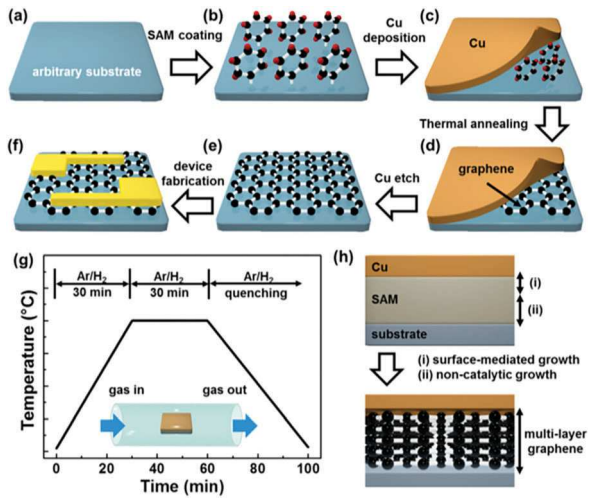

Fig. 16 Schematic of the transfer-free graphene growth procedure illustrating: (a) the target substrate; (b) phenyl-SAM coating on the prepared substrate; (c) Cu thin film evaporation on the SAM-coated substrate; (d) graphene growth between the Cu layer and the target substrate by thermal annealing; (e) selective Cu etching; and (f) the graphene-based device after contact metal deposition; (g) Graphene growth temperature as a function of time (the inset is a schematic of the horizontal tube furnace); (h) Schematic of the growth mechanism for multilayer graphene. Reproduced with permission from ref. 72. Copyright 2016 American Chemical Society.

There are various mechanisms for direct preparation of high-quality graphene on dielectric substrates.[70] Lately, a transfer-free growth of multilayer graphene on various substrates such as SiO_2/Si, quartz, GaN, and textured Si has been achieved following the mechanism of annealing-based capping-metal-catalyzed synthesis.[70,71] In this approach, a SAM layer is coated on the target substrate followed by Cu deposition. After graphene growth is achieved during thermal annealing, the metal catalyst layer is removed leaving graphene on the substrate as illustrated in Fig. 16.[72]

In addition, the direct growth of bilayer graphene (BLG) on insulating substrates (SiO_2, h-BN, Si_3N_4 and Al_2O_3)[73] and single layer single-crystalline graphene on h-BN have been demonstrated.[74] Despite the exciting progress, the growth of wafer scale single crystal graphene on insulating substrates remains a challenge.[70]

3. Conclusions and outlook

Rapid advances have been made in the transfer of CVD graphene onto dielectric substrates. The support layer has developed from hard-to-remove expensive polymers (PMMA, PDMS, thermal release adhesives)[5,11,37,48,52] to cost-effective environmentally friendly natural polymers (cellulose acetate, agarose),[57,64] from polymer to non-polymer,[58,59,64] from solid to liquid-based,[67] and from tangible to intangible.[68] As the support layer has a strong effect on the electronic properties of graphene, it is expected that the next generation support layers will be residue-free, flexible, cost-effective, environmentally friendly, and reliable. Apart from selecting abundant graphene carriers, recycling of the substrates is a very important step in reducing the transfer cost.

Each graphene transfer method possesses unique characteristics and the selection of a transfer technique largely depends on the application. For example, the roll-to-roll transfer method is suitable for mass production of graphene on flexible substrates for transparent electrodes, while the support-free technique is superior for the study of graphene chemistry. Just as no solvent can universally dissolve any substance, there is no unique graphene transfer method that can fill all purposes.

Future developments in graphene transfer will continue to move towards low cost, scalability, and simplification until the growth of large area single-crystal graphene films on substrates of interest becomes a reality. Nevertheless, graphene transfer will remain the only alternative for a number of applications, especially those involving plastic substrates, which cannot withstand the high temperatures required for the CVD growth of graphene.

Conflicts of interest

There are no conflicts to declare.

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