The Transfer of Graphene: A Review

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Abstract. Graphene is a two-dimensional atomic crystal which presents amazing properties. Several techniques for graphene synthesis were developed since the first studies and the most used methods are presented in this work. Moreover, recent progress in graphene transfer and its effects on the graphene quality are reviewed.

Keywords Graphene, Growth, Transfer, Pollution, Residues

1 Introduction

The first mention of graphite appeared in 1840 by the Dr. Schafhaeutl who observed large graphite layers “or laminae” [1]. The term graphene is purpose for the first time by Boehm et al. in 1986 after many works about reduced graphite oxide [2,3]. In 2004, Novoselov, Geim and co-workers had insulated graphene to characterize it impressive properties [4].

Graphene is a two-dimensional (2D) material composed by single layer of carbon atoms tightly bound in a honeycomb lattice [4]. Currently, research interest in graphene is really important because of its unique mechanical [5,6], optical [7] and electronic [8-11] properties [12] and could be used for flexible electronics [13], high frequency transistors [14,15], logic transistor [16], photodetector [17] and sensors [18].

The electronics properties of graphene are unusual: it is a zero band gap semiconductor [4,19,20], which displays an ultrahigh mobility at room temperature of 200 000 cm²V⁻¹s⁻¹ [21]. Moreover, the quantum Hall effect (QHE) can be
observed at room temperature because electrons in graphene behave as massless relativistic particle [19,20,22]. Optical properties of graphene are attractive because its transparency is c.a. 97.7% [23]. Coupled with its impressive mechanical properties, Young modulus of 1.0 TPa and fracture strength of 130 GPa [12], it represents an exciting material for flexible transparent electronic and organic light-emitting diodes (OLED), for instance [24].

First synthesis of graphene was followed by transfer, using a scotch tape, to SiO$_2$ layer on top of Si wafer in order to study it [4]. Because the graphene could be used in lots of different applications, transfer of graphene is an easy and successful way to obtain graphene on various substrates such as oxide [4,25] or polymer [26]. Different strategies are pursued to improve the quality of graphene after transfer [27].

In this review, growth and transfer of graphene will be described and the influence of the transfer process on graphene properties will be discussed.

2 Growth of Graphene

Graphene is a material recently isolated and studied by Novoselov and Geim in 2004 [4]. However, different ways of synthesis of this attractive material have been developed. In this section, ways of synthesis of graphene are briefly described and discussed.

2.1 Micromechanical cleavage of graphene

This technique was used by Novoselov et al. for the first synthesis of graphene and study of its properties [4]. The first micromechanical exfoliation of graphite was realized in 1999 [28,29]. At the beginning, Lu et al. used a razor blade to cleave thick plates of Highly Oriented Pyrolytic Graphite (HOPG) into 1.5 mm thick pieces. Plasma Enhanced Chemical Vapor Deposition (PECVD) was used for the deposition of a SiO$_2$ film (200 nm) onto the cleaved surface and then a positive photoresist was spun coated. After photolithography and removal of the SiO$_2$ film in Hydrogen Fluoride (HF) solution, an oxygen plasma etching was performed.

The same kind of process was used by Novoselov et al. and they used scotch tape to peel flakes of graphite off the substrate [4]. This method is again used more recently [30,31] because it is a well-known technique to obtain graphene with very few defects [4,27,32,33]. However, micromechanical exfoliation of graphene flakes is able to produce sheets of limited size (< 1 mm$^2$) and thus cannot be considered promising for commercial production and application [24,27,32-36]. That is why other preparation methods have been developed.
2.2 Epitaxial graphene on SiC

In 1998, Forbeaux et al. annealed silicon carbide under vacuum to obtain monolayer of graphite [37]. Due to the high interest for graphene, Berger et al. used this technique in 2004 to prepare ultrathin films of graphene [38]. The principle of growing of graphene by this method is simple: under ultrahigh vacuum and high temperature, silicon on the top of the compounds desorbs and only few layers of graphene are left.

Differences between graphenes prepared by micromechanical exfoliation and epitaxial methods were observed [38-40]. Wang et al. studied by Raman spectroscopy monolayer of graphene prepared by micromechanical cleavage of graphite deposited on various substrates and epitaxial monolayer graphene grown on n-type Si-terminated 6H-SiC (0001) and observed differences in the G-, D- and 2D-bands position. These differences are attributed to electron doping transferred from the SiC [41,42] and the strain effect caused by the substrate [43]. The number of graphene layers obtained with this kind of synthesis can be determined by Si:C Auger intensity ratio [39].

Although this technique is relatively easy, synthesis of graphene on silicon carbide is expensive because of the cost of the SiC wafers and the high temperature and vacuum required. Moreover, the quality of graphene is lower than that obtained by micromechanical cleavage of graphite and involves different properties which could be interesting for specific application such as electronics [14,16,24,42,44].

2.3 Chemical vapor deposition

Chemical Vapor Deposition (CVD) is a widely used preparation process for thin film materials. In 1994, CVD was used by Johansson et al. to produce few layer graphite [45]. For this process, graphene is synthesized by catalytic decomposition at high temperature of carbonated gases, such as methane or ethylene for instance, on a metal, most used are copper and nickel.

Since 2002, Obraztsov et al. used this technique for the synthesis of nanosized graphite crystallite, carbon nanotubes and graphene [46,47]. Plasma was used to assist CVD in order to modify some CVD parameters, substrate temperature for instance [48,49]. Table 1 presents a non-exhaustive list of different chemical vapor deposition processes employed for graphene preparation. The mostly used substrates in a CVD process are Cu and Ni, but other metals were employed [50,51] such Ir(111) [52], Co(0001) [53], Pt(111) [54], Pd(111) [55,56], Au(111) [57], Ag(111) [58], Rh(111) [59], Ru(0001) [60]. Nevertheless, the graphene synthesis can be realized catalyst-free on various glass substrate, such as quartz or colored glass [61].

These different processes are really interesting because different temperature
Table 1. Utilization of different kind of CVD for graphene synthesis

<table>
<thead>
<tr>
<th>Type</th>
<th>Substrate</th>
<th>$T_{\text{sub}}$ ($^\circ$C)</th>
<th>Gases</th>
<th>$P_T$ (Torr)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC-CVD</td>
<td>Si, Ni</td>
<td>950</td>
<td>H$_2$/CH$_4$ (92/8)</td>
<td>80</td>
<td>[47]</td>
</tr>
<tr>
<td>RF-PECVD</td>
<td>Ni, Si</td>
<td>600-950</td>
<td>H$_2$/CH$_4$ (95/5-0/100)</td>
<td>20x10$^{-3}$-400x10$^{-3}$</td>
<td>[197]</td>
</tr>
<tr>
<td>LP-CVD</td>
<td>Ir (111)</td>
<td>847, 947, 1047</td>
<td>C$_2$H$_4$</td>
<td>7.5x10$^{-10}$</td>
<td>[52]</td>
</tr>
<tr>
<td>CVD</td>
<td>Cu</td>
<td>850, 900, 950</td>
<td>CH$_4$</td>
<td>50</td>
<td>[198]</td>
</tr>
<tr>
<td>EBEP-CVD</td>
<td>Si (100)</td>
<td>570</td>
<td>H$_2$/CH$_4$</td>
<td>15x10$^{-3}$-30x10$^{-3}$</td>
<td>[199]</td>
</tr>
<tr>
<td>MPECVD</td>
<td>Si</td>
<td>550</td>
<td>H$_2$/CH$_4$ (100/5)</td>
<td>1.65</td>
<td>[200]</td>
</tr>
<tr>
<td>CTCVD</td>
<td>Cu</td>
<td>1010</td>
<td>H$_2$/CH$_4$</td>
<td>4</td>
<td>[201]</td>
</tr>
<tr>
<td>APCVD</td>
<td>Cu</td>
<td>1075</td>
<td>H$_2$/CH$_4$</td>
<td>atm</td>
<td>[202]</td>
</tr>
</tbody>
</table>

$^a$ Direct Current Discharge CVD
$^b$ Radio Frequency – Plasma Enhanced CVD
$^c$ Low Pressure CVD
$^d$ Electron Beam Enhanced Plasma CVD
$^e$ Microwave Plasma Enhanced CVD
$^f$ Concentric Tube CVD
$^g$ Atmospheric Pressure CVD

range was used, from 380 to more than 1000$^\circ$C. Moreover different kind of carbonated source methane or ethane can be used, such as ethylene [62], propylene [63], methanol [64], ethanol [64], 1-propanol [64], acetylene [65], graphene [66] and an unusual precursor like sugar (C$_{12}$H$_{22}$O$_{11}$) can also be used [67].

Chemical vapor deposition is very advantageous because various substrate and precursors can be used, but this technique is expensive. Indeed, energy consumption is high and after growth the substrate often needs to be etched completely to transfer graphene. However, large area uniform graphene films are produced with high quality [68,69] and with reduced consumption cost with MPECVD for instance, this process will be more used for graphene synthesis [24].

2.4 Liquid phase exfoliation of graphite

Stable colloidal suspension of graphene sheets can be obtained by liquid phase exfoliation. In this method, graphite is dispersed in a specific solvent in order to surmount the graphene-graphene interlayer Van der Walls interaction [70]. The solvent used are generally non aqueous [71], for instance DMF [72], N-methylpyrrolidone [73] or pure hydrazine [74], but aqueous solution with surfactant [70,75] or without [76] can also be used.
Liquid exfoliation of graphene is an interesting route of graphene synthesis because it is enough simple and one of the cheapest ways. However, the low quality of graphene, with several layers, allows only specific applications [24].

2.5 Others grows methods

Principal ways of the graphene synthesis have been described but several interesting methods will be presented in this section. These methods are connected with one or more of the principal ways and certain advantages are attractive for research and maybe scale-up for applications.

2.5.1 Electrochemical exfoliation of graphite

Electrochemical exfoliation of graphite is a method close to the liquid phase exfoliation coupled with an electrochemical device, a schematic diagram of this process is described in Figure 1. This process was used in 2008 by Liu et al. in order to synthesized ionic liquid functionalized graphene sheets [77]. Lu et al. ascribed the mechanism of exfoliation to the anionic intercalation from the ionic liquid, used as an electrolyte, coupled to the anodic oxidation of water [78]. Ionic solution from sulfuric acid and water was used by Su et al. as an electrolyte to synthesized high quality graphene for ink applications [79].

![Schematic diagram of electrochemical exfoliation of graphite from [77].](image)

This cost-effective process is easy to use but the graphene qualities and sheets size allow only niches applications.

2.5.2 From polymer

Graphene can be grown from a solid carbon source annealed: vinyl polymer. In this method developed in 2011, the polymer is spin coated on the SiO$_2$ substrate. Next, a nickel film is deposited on top of the polymer film and afterwards annealing at 1000°C followed by Ni etching, 2 layers [80] or 3 layers [81] of graphene are then observed on the substrate. The vinyl polymers used are
polystyrene (PS) [80,81], poly(methyl methacrylate) (PMMA) [80,81], poly(2-phenylpropyl)methylsiloxane [80], poly(acrylonitrile-co-butadiene-co-styrene) (ABS) [80] or polyacrylonitrile [81]. Yan et al. used also a self-assembled monolayer of butyltriethoxylane atop a SiO$_2$ layer [80]. This approach improved on the works presented in 2010 by Zheng et al. which used amorphous carbon as a carbon source, deposited on the substrate by electron-beam evaporation [82]. The same kind of process is used by Peng et al. but the nickel film is deposited directly onto a SiO$_2$ substrate followed by the spin coating of polymer [83]. After annealing at 1000°C, bilayer graphene formed by carbon diffusion through Ni film and few layers graphene on top of the top of the material are observed. Etching treatment is used to remove the few layers graphene and Ni film. Carbon sources can be PMMA, high impact polystyrene, ABS or gas flow of methane. These closed methods are interesting because high quality graphene is obtained without a transfer process neither explosive gases. Moreover, the amount of feed carbon is fixed which entails better control of graphene thickness which is not easy in the CVD method. These accessible ways of graphene growing need only high temperature, so operation cost will probably be improved and the process developed in the future.

2.5.3 3D graphene

In this last section, the subject will not be only graphene growth but more focus will be placed on 3D-graphene. This material is very promising and different synthesis approaches are studied.

From nickel foam, 3D-graphene can grow by CVD. In order to avoid graphene network collapsing, a thin layer of PMMA is deposited on the graphene/Ni structure. After Ni etching followed by PMMA dissolving, 3D-graphene is obtained [84-86]. However, 3D-graphene can be synthesized without support like PMMA [87].

Others ways of synthesis of 3D-graphene such as hydrothermal gelation synthesis [88], colloidal-sphere synthesis [89] and others template and templateless techniques [33] are developed by researchers spurred by the interesting properties of 3D-graphene.

Indeed, this structure is attractive in comparison to plane graphene which exhibits low specific area due to the two-dimensional structure and an irreversible agglomeration induced by the $\pi-\pi$ interaction and Van der Walls forces between layers of graphene. Moreover, 3D-graphene has attractive properties for high energy storage application [89] or enzymeless glucose detection [90].

Graphene is an amazing materials and lot of researchers investigate different ways of synthesis since it characterization in 2004. Each described methods present advantages and drawbacks and Novoselov et al. determine in 2012 an interesting equilibrium between graphene qualities and surface synthesized [24].
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Indeed, best graphene quality is obtained with micromechanical cleavage, but the area prepared is extremely reduced and unthinkable for industrial application. On the other hand, liquid phase exfoliation is a cheap way to easily prepare graphene but the quality is low. Finally, between best and reduced graphene quality, epitaxial graphene on SiC and CVD are two methods which provide high graphene quality and the possibility to synthesize it on large area. However, the cost of these processes is high enough to justify the efforts of lots of researchers trying to reduce this by developing others methods.

Finally, the growing method used involve specific substrates and for the purpose of characterization or making a new device, graphene had to be transferred and lots of transfer processes were developed which will be presented and discussed in the next section.

3 Transfer of Graphene

The different growing method involve one kind of substrate, for instance metallic substrate to grow graphene by CVD or graphite substrate by micromechanical cleavage, while often a different one is needed to measure its properties or for a particular application.

Here the different transfer processes come into play. Thereby graphene is transferred on many substrate such as oxides (SiO$_2$ [4], Al$_2$O$_3$ [25], WO$_3$ [91]), polymers (polyethylene terephthalate (PET) [92], polydimethylsiloxane (PDMS) [93], polystyrene [94], polyimide (PI) [95]), metallic substrates (Au [96], Ti [97], NiFe [43], Ag nanostructure [98], Li [99]) and others various substrates (boron nitride [100], SiC [101], Si$_N_x$ [102], sapphire [103], fiber [104], InAs/GaAs [105], KBr [106] or graphene [107]). Graphene can likewise be transferred on structured substrate such as holey TEM grids [108], wells substrate [109] or perforated substrate [109].

In the following section, transfer techniques will be presented and discussed.

3.1 Polymeric layer

After growth on a substrate, graphene can be isolated by substrate etching. However, a single layer of graphene is so thin that perfect transfer without cracks or defect is extremely hard. To reduce this problem, Reina et al. in 2008 used a polymeric layer deposited on the graphene/substrate film by spin coating and, after substrate etching, manipulate it more easily [110].

Because this technique is very simple to use, cheap, available on various substrate and graphene obtained is quite similar than after growing, this is the most employed method for graphene transfer.

Figure 2 presents the transfer process using a polymer layer presented by Reina et al. In the first step, polymeric layer, PMMA in this case, is spin coated on
Figure 2. Schematic diagram of the transferring process. The graphene sheets are deposited on SiO$_2$/Si substrates (300nm thermal oxide) via HOPG microcleaving and are finally transferred to a nonspecific substrate from [110].

graphene grown on the substrate. Then, this material is put in a solution in order to etch the substrate which leaves the PMMA/graphene freestanding. This layer is washed in water and, in the third step, is deposited on a new substrate. Finally, the polymer layer is dissolved in acetone to obtain graphene deposited on a desired substrate.

This technique is powerful for graphene growth by CVD on a metallic substrate, such as Cu or Ni, which can be easily removed.

Schematic diagram of the transferring process. The graphene sheets are deposited on SiO$_2$/Si substrates (300nm thermal oxide) via HOPG microcleaving and are finally transferred to a nonspecific substrate from [110].

3.1.1 Poly(methyl methacrylate)

Transfer with PMMA is the most employed technique because PMMA is easy to manipulate and cheap. To our knowledge, only three PMMA solvents are used: anisole (2% [108], 4 vol.% [111], 5% [101], 6–9 wt.% [110], 8 wt.% [112] or 50% [113]), chlorobenzene (3% [114], 10% [99], 20 mg/ml [109] or 46 mg/ml [115], 50 mg/ml [116]) and toluene (4 wt.% [117]). The influence of the PMMA solvent on the graphene quality was studied by comparing the electrical conductivity and amount of PMMA residues in graphene for 10, 40 and 80 mg/ml of PMMA dissolved in chlorobenzene [118].
However, more types of stamp dissolver could be used. Acetone, around 55°C for 2 h [36], “warm” [64], “hot” [119], “boiling” [120] or an acetone flow [110] and thermal heating (450°C – 90 min – H₂/Ar (700/300 sccm) [113], 350°C – 3–4h – in air [108], 350°C – ~2 h – H₂/Ar (500/500 sccm) [109], 400°C – ~1 h – H₂/Ar (500/500 sccm) [121] are the most employed stamp dissolvers. Acetone and heat treatment (480°C – 1 h – H₂/Ar) can be coupled [122] and Park et al. compared the acetone and heat treatment to remove the PMMA layer [123] because trichloroethylene vapor or solvent can also be used [105]. PMMA can also be dissolved in toluene [124] and dichloromethane [125].

The substrate has to be etched and different etchants are used in relationship with the nature of the substrate. For copper foil, various compounds are employed:

- Ammonium persulfate (0.05M [126], 0.1M [127], 0.2M [128], 0.5M [129], 0.05 g/ml [117], 1 wt.% [130] or previously dipped in 3:1 water : HNO₃ for 1 min [131])
- Ammonium sulfate (0.1M [114])
- Iron (III) chloride (0.4 g/ml [98], 0.5M [132], 1M [133])
- Iron (III) nitrate (0.05 g/ml [134], 0.7M [111])
- H₂O₂ (3%) / HCl (35%) (3:1) [135]
- Iron (III) chloride (0.25M) followed by HF (10%) [136]
- Mixed solution of CuSO₄ (0.5 mM/ml) and HCl (3M) [137]
- Marble’s reagent (CuSO₄/HCl/H₂O: 10 g/50 mL/50 mL) [67]
- Commercial etchant from Transene: 49-1 [138], CE-100 [139], CE 100/200 [108], CE-100 followed by HCl (10%) [140], CE-100 followed by HNO₃ (10 min) [123].

For the etching of nickel foil, these etchants are used:

- Hydrogen Fluoride solution [141]
- Hydrochloric acid (3w.% [142], 15% [82])
- Nickel etchant from transgene 90°C – 2 h [143]

To etch silicon oxide layer, sodium hydroxide (1M – 90°C) [110] and potassium hydroxide [144] could be used.

The use of PMMA to protect graphene layer is an easy technique for the graphene transfer and many researches try to improve this process. In 2009, Li et al. spin coated a second layer of PMMA deposited on the first layer washed in water to prevent cracks observed with only one layer of PMMA. During this second deposition, a liquid PMMA solution was added to the first layer in order to dissolve the precoated PMMA. That involves mechanical relaxation at the connection between PMMA and graphene layer which can be transferred more easily without cracks and tears [134]. In 2011, Suk et al. baked at 180°C for 3 h the new substrate before the PMMA removing step to improve the graphene adhesion and its quality after transfer [109].
Moreover, transfer of graphene is used to control accurately the number of graphene layers or for depositing graphene layer by layer. Thereby, bilayer [107] to quadrilayer [145], quiquelayer [146] and sexalayer [147] were fabricated for specific applications.

3.1.2 Polydimethylsiloxane

The main difference between both polymers is that PDMS is used as a stamp. This technique is really suitable but needs stronger adhesion between the graphene and the new substrate than between the graphene and the PDMS stamp. This limitation has caused little utilization of this polymeric layer alone for graphene transfer; indeed, to our knowledge, this technique is used to transfer graphene on SiO$_2$ [148].

3.1.3 Others polymer

Various polymer or combination thereof are used for the graphene transfer process:

- Polycarbonate film (Poly(bisphenol A carbonate)) [149] in the same way as PMMA but the transfer is cleaner, with less polymer residues.
- Silicone rubber (polymerized siloxanes) to transfer graphene to a glass plate [150].
- Polyimide (PI) to peel off the graphene from various substrate. Moreover, this PI/graphene film is interesting for flexible electronic devices [151].
- PDMS can be deposited as an extra supporting layer on the PMMA/graphene in order to obtain transferred graphene with few defects and low impurity doping [152].
- A PDMS block can be pressed on a PMMA layer to manipulate the graphene layer easier [109].
- PMMA/Cellulose Acetate Butyrate (CAB) for a minimal residue graphene transfer [96].
- Polyethylene terephthalate (PET)/silicone layers to transfer more efficiently large area graphene films [153].
- A water-soluble layer (Mitsubishi Rayon aquaSAVE)/PMMA to transfer graphene on boron nitride [154].
- Poly(isobutylene) (PIB)/PDMS to transfer graphene on SiO$_2$/Si wafer [155].
- PS/PDMS to transfer graphene on SiO$_2$/Si wafer [155].
- Teflon AF2400 (DuPont Fluoroproducts)/PDMS to transfer graphene on SiO$_2$/Si wafer [155].
- Commercial polymeric layer can be used, for instance GelPak® polymer film (DGL-20-04, Gel-Pak, Delphon) to transfer graphene on PI [156] or...
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CYTOP® (fluoropolymer from Asahi Glass) to simultaneously transfer and dope graphene [126].

- A mixture of silicon based adhesive solution can be spin coated on graphene. This pressure sensitive adhesive film (PSAF) is next peeled-off the substrate [157].

Lots of polymers are used but the huge majority of these transfers using PMMA. However, because some residues are observed after transfer with this material, others polymers are investigated for this purpose in order to obtain better graphene quality.

### 3.2 Thermal release tape

The first use of a scotch tape to peel off the graphene was by Novoselov *et al.* but to make the transfer easier, a commercial product is really efficient. Thermal release tape (TRT) is a kind of adhesive tape which can be handily released by heating which eliminates the adhesion strength of the tape. TRT from Jinsung Chemical Co. [13] and Nitto Denko Co. was used [158].

The use of thermal release tape is easy, fast and suitable for large area transfer but voids and some residues from TRT can appear after the transfer, including p-doping of the graphene [157].

### 3.3 Free floating

Transfer by free floating is the easiest transfer technique. Indeed, after graphene growth, the material is placed in a solution in order to etch the substrate. After etching graphene sheets float on the solution surface. These are captured on the top of the new substrate [159-162] or by extraction of the solution to adjust the graphene landing on the target substrate [128].

To improve contact between the surface and the graphene sheets, isopropanol [163,164] or chloroform [165] could be used. Indeed, the surface tension of these solutions brings about close contact after evaporation.

Transfer by free floating is the most accessible method, fast, cheap and without contamination. However, during the transfer process, more cracks or voids could appear, for this reason, most transfers are made with a protective layer.

### 3.4 Bubble transfer

The bubble transfer is an electrochemical process where hydrogen bubbles are formed at the metallic substrate/graphene interface (Figure 3). A protective layer, for instance PMMA or PC [166], is deposited on the graphene and after applying electric field between the growth substrate, used as a cathode, and the anode in an electrolyte (NaOH (0.25M) [166], (1M) [167], Na₂SO₄ (0.5M)
[168] or K$_2$S$_2$O$_8$ (0.05mM) [169]), formation of H$_2$ bubbles causes the detachment of graphene/PMMA. Cu [169] and Pt [167] was used as a cathode but the use of Cu or Ni as a cathode causes partial dissolution of the metal during the electrochemical process while the utilization of Pt foil permits to re-use this foil for CVD growing [54]. Bubble transfer can be used for the transfer of large scale graphene from Ir to Si/SiO$_2$. To do this, tetraoctylammonium ions were intercalated between graphene and Ir and then, a PMMA layer was coated on the graphene to protect it [170]. After the detachment, graphene/protective layer were deposited on the new substrate and the polymeric layer was dissolved or thermally annealed.

The bubble transfer is quite simple and leaves less metallic residues than transfer with a polymer layer because it avoids the etching step. However, the use of a protective layer leaves carbonated residues and consequently modifies the graphene properties.

3.5 Transfer by pressing

By direct pressure between graphene and a target substrate, the graphene layer can be transferred and there are several techniques used pressing method to transfer graphene:

- Graphene could be transferred from Si/SiO$_2$ to PET by pressing at 170°C at 1500 psi. Under these conditions, the glass transition temperature of PET is reached which improves the transfer quality [92].
- By pressing a stamp coated with a “transferring-layer”, a resin based ma-
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material spin coated on the stamp surface, on HOPG at room temperature and 300 psi for 4 min, the graphene layers are transferred [171].

- After processing in O\textsubscript{2} plasma, SiO\textsubscript{2}/Si substrate is pressed with graphene/Ni for hours. With this method, some of the graphene flakes are transferred on the new substrate [172].

- After growth, the Cu/graphene is put in water onto the wafer surface. With mild pressure during 10 h, these materials are sandwiched between two glass slides in a beaker containing 1.5 L of water ($\approx$ 15N) [173].

- Graphene growth on Cu is transferred to a PET substrate using hot press lamination followed by copper etching in iron chloride solution [26].

- Lock et al. modified a polystyrene substrate by plasma to enhance the graphene adhesion. The functionalized surface was placed in contact with graphene/Cu at 500 psi during 30 min using a NX 2000 Nano Imprinter [94].

- Graphene growth on Cu was put on a cellulose acetate substrate and pressed at $\approx$ 200°C followed by copper etching [174].

The techniques reviewed here are interesting but there are not enough studies about the transferred graphene quality for these different methods. However, with some, good quality graphene could be obtained after the transfer [175].

3.6 Mixing of techniques

For transfer, different techniques could be used together in order to improve the quality or the ability of the graphene transfer.

Metallic layer and TRT transfer techniques could be joined for the graphene transfer. So, Song et al. deposited a gold film onto a patterned HOPG disk and used a TRT to peel off the gold film with graphene patterns. The graphene transfer is made by contact with a silicon wafer at 180°C for 5 min. Under these conditions, the TRT is removed to the gold layer which is finally etched in a gold etchant solution (from Transene) [34].

A metallic layer deposited on the graphene associated with a polymeric layer spin coated on the metallic film could be used. Huang et al. made the deposition of a gold film on the graphene grown on Si wafer. Polyvinyl alcohol (PVA) is then cast on these films and, after solidification, peeled off from the wafer. The film is transferred onto PDMS and PVA is rinsed with DI water and the gold layer is etched [93]. This technique is also employed with Au and Pt as metallic layer and PI as polymer layer [176].

A polymeric layer could be used to protect the graphene layer combined with TRT to remove these layers more easily. So a PDMS stamp and a TRT could be attached to the graphene films grown on Cu or Ni precoated on Si/SiO\textsubscript{2} [177]. These layers are soaked in water to detach the metallic layer from SiO\textsubscript{2} and then
Beck et al. made a stamp from PDMS coated with parylene-c and a fluorinated photoresist based on 1H,1H,2H,2H-perfluorodecyl methacrylate (FDMA) and tert-butyl methacrylate (TBMA). Graphene grown on copper is laid on this material, with the graphene-side touching and uniform pressure applied, then the copper layer is etched. The new substrate is constituted of an organic semiconductor (2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBi)) deposited on ITO coated glass. Graphene is transferred by a light pressure of the stamp on the substrate heated at 50°C to promote adhesion. After 30s, stamp is lifted away and the residual fluorinated photoresist is removed with a specific solvent. This technique is really interesting for the graphene transfer on organic surface for Organic Light Emitting Diode (OLED) or Organic Photovoltaic (OPV) application for instance [179].

With the roll-to-roll technique, patterned graphene could be swiftly transferred from Cu foil to the target substrate [180]. This method is interesting for the industrial production of good quality graphene.

3.7 Other techniques

Lots of techniques are efficient for the graphene transfer and the most employed use protective polymeric layer. However, other chemical compounds could be used as a supportive layer. Cyclododecane is spin coated on graphene grown on Cu and used as a protective layer to make the graphene transfer [181]. Pentacene was placed using an organic molecular-beam deposition onto graphene/Cu. Copper foil is etched in ammonium persulfate solution and pentacene/graphene is moved onto the new substrate. The pentacene layer could be removed by thermal annealing at 250°C, which involves doping of the graphene layer, or by immersing in tetrahydrofuran (THF), which leaves undoped graphene [182]. Substitution of polymeric layer by organic compounds is an interesting way for the graphene transfer but there is not enough studies for now about the transferred film quality and the works had to be investigated.

Graphene is a promising material with amazing properties. The ability to manipulate it easily is really important for many application and a non-exhaustive list of transfer techniques have been described in this section. However, these techniques present inconveniences and Table 2 summarizes the main ways of
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Table 2. Defaults of graphene due to the transfer method

<table>
<thead>
<tr>
<th></th>
<th>Tears</th>
<th>Voids</th>
<th>Organic residues</th>
<th>Metallic residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric layer</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>TRT</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>Free floating</td>
<td>✓ ✓ ✓</td>
<td>✓</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Bubble transfer</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
</tbody>
</table>

graphene after transfer. So, the best way to avoid residues on graphene is free floating but this technique causes defaults of the graphene structure. In the same way, to keep good uniformity of the graphene, the techniques used leave some residues on the material.

4 Influence of the Transfer Process on Graphene

The transfer of graphene is an important process making it possible to use it easily on various substrates. However, during this process, some alterations can modify the graphene properties because the different transfer techniques present drawbacks. On one hand, graphene contains surface modifications such as holes, during transfer by free floating for instance or, on the other hand, impurities can contaminate graphene when PMMA is employed for instance. Many researches are focused to reduce and avoid these modifications and the following section reports these works.

4.1 Surface modification

Transfer of graphene involves surface modification such as wrinkles, tears, or cracks. Figure 4 presents some defects observed with optical microscope or scanning electron microscope on graphene transferred by different methods.

Figure 4. (a) optical micrograph of graphene transferred on SiO$_2$/Si using PMMA from [134], (b) optical and (c) scanning electron microscope image of graphene transferred on SiO$_2$/Si using roll-to-roll process from [175].
Interactions between cracks and the thermal annealing process were observed [103].

4.2 Pollution of graphene

Wet transfer with polymeric layer is the most used technique for the transfer of graphene but this process involved some contamination, cracks, voids or tears. First of all, the polymeric layer is used to limit the graphene damage but the protective coating and the etching step can be a source of contamination [183]. Poly(methyl methacrylate) is the most employed protective layer and some researches about the graphene contamination from PMMA were published. Indeed, PMMA leaves residues which involve defects on graphene and degradation of its electronic mobility [181]. Graphene samples were studied by XPS before and after the transfer process using PMMA [184]. In this study, two chemical bonds (286.5 and 289.1 eV) associated with the bonding of carbon atoms in polymer backbone and the methoxy function group respectively, are observed after transfer. Another peak at 287.4 eV associated with the carboxyl function group can be detected [185].

The p-doping effect is due to the oxygen groups on the graphene surface which act as holes acceptors (epoxy, ether...). An easy way to observe hole-doping of graphene is the study of G and 2D bands, which are at 1580 and 2670 cm\(^{-1}\) respectively, for pristine graphene with Raman spectroscopy. After transfer by PMMA or TRT, upshifted values were registered implying hole-doped graphene, whereas n-doped graphene has a downshift in the G band and an upshift in the 2D band [186].

Metallic contamination of graphene can appear during the graphene growth and/or the etching step. Prusa et al. observed a total coverage of metal impurities such as Fe, Sn, Na during both step up to 50% of a monolayer [187]. The most common catalyst for CVD process are Cu and Ni and compounds used to etch them contain metallic ions. The strong oxidation power of metal etchants involves possible oxidation of graphene and also contamination of graphene from the etchant [188]. For instance, the use of FeCl\(_3\) or Fe(NO\(_3\))\(_3\) leave metallic impurities, Fe and metal substrate undissolved in the transferred graphene which will modify it electrochemical properties [189]. The part from the metallic substrate can be reduced with a long time etching but involve increased risk of cracks [190]. To avoid contamination from the growth substrate Cu, Costa et al. suggest to use monocrystalline Cu(100) or Cu(110). Indeed, they studied the graphene grown by CVD on Cu(100), Cu(110) and Cu(111) through heat treatment. They observed weak interaction between graphene and Cu(100) and Cu(110) surfaces and close contact with Cu(111), that’s involve some problem during the transfer of graphene from polycrystalline copper foil [191]. In the same way, graphene grown on Cu(100) and Cu(110) is either not or weakly doped whilst graphene grown on Cu(111) is n-doped [192].
4.3 Improve transfer using polymeric layer

Several techniques were developed to limit this contamination by using different steps or others polymer than PMMA. An extra layer of PDMS can be deposited on PMMA/graphene to obtain fewer defects and low impurity doping [152]. Dekar et al. developed an “improved wet transfer process” with this regard [101]. This method is composed with 3 steps, in the first one, PMMA deposited on graphene is baked at 170°C and slowly cooled at room temperature, for the etching step, an aqueous (NH$_4$)$_2$S$_2$O$_8$ solution is used during 15h to avoid metallic contamination. Finally, it is manipulated with wipers to remove water between graphene and the new substrate in order to prevent a water channel which could be a source of cracks or folds in the graphene and the film is exposed to deep UV, followed by dissolution in methyl isobutyl ketone and finally in warm acetone to remove PMMA layer. Other polymers such as poly(bisphenol A carbonate) can be deposited to reduce contamination from PMMA [149]. The amount of polymer residues left after the transfer process using PMMA is connected with the initial concentration of PMMA. Actually, a solution with a lower concentration gave less residue after PMMA removal with acetone which caused less p-doping in graphene [118]. To compensate initially p-doped graphene from PMMA residues, the graphene can be exposed to a solution of formamide [118]. Finally, substitution of water by isopropyl alcohol for the wet transfer with polymeric layer is an interesting method to reduce impurities or defects and obtain, after heat treatment, comparable electrical properties with exfoliated graphene on SiO$_2$ [129].

4.4 Improve transfer using others transfer techniques

A few methods improve transfer techniques to enhance the graphene quality. Dry transfer based on a hot pressing method of TRT on graphene was developed instead of the roll to roll technique which leads to some cracks and voids on the graphene [175]. This approach allows for better mechanical and electrical properties of the transferred graphene. A pressure sensitive adhesive films (PSAF), based on silicone pressure sensitive adhesive, can be used to substitute transfer using PMMA and TRT [157]. By soft pressure of PSAF on graphene followed by peel-off, less ripples and residues are observed and this graphene is less p-doped than graphene transferred using TRT or PMMA and presents better electronic properties. The direct transfer technique is improved by Regan et al. by dropping the target substrate deposited on the structure graphene/Cu in an isopropyl alcohol solution [183]. The aim is to draw graphene and substrate into intimate contact during the alcohol evaporation [193].
4.5 Removal of impurities

Different techniques are used to avoid or limit contamination but other processes were developed to remove the impurities.

To eliminate partially or totally PMMA, Pirkle et al. compare, in their study, the influence of heating after PMMA dissolving in acetone. This heating step (300°C for 3 h in UHV) allows a better PMMA removal and uniformity of the surface [131]. In the same way, Park et al. study the PMMA removal with acetone, annealing and both and they observed the cleanest graphene surface with the use of acetone vapor, acetone immersion and annealing [140] but a single heat treatment may not be enough for the clean removal of PMMA [123] although recent studies use heating treatment coupled with acetone to remove PMMA with less residues [194]. However, this annealing involves blue-shifted G and 2D peaks, so the structure is more p-doped [131,138].

To remove residues left on the transferred graphene, Joiner et al. used a thin metallic layer of Ti deposited by thermal e-beam evaporation. This technique had no influence on the graphene quality but removed totally residues observed on the graphene [195]. To remove residues and the unwanted doping due to the transfer process and restore the pristine state, low density inductively coupled plasma (5W ICP) of argon can be used [196].

The transfer of graphene is accompanied by degradation of its quality. Graphene surface can be modified during transfer and cracks, tears and holes can appear in the transferred graphene. Moreover, depending on the technique used, some residues can be left on the graphene. These modifications have important influence on the graphene properties. In order to reduce these alterations some interesting works are focused to limit the source of residues by using an etchant without metallic ions for instance, or to remove them with techniques such as low density inductively coupled plasma.

5 Conclusion

Graphene is a promising material which presents amazing properties. In this work, different ways of synthesis were described and discussed and different graphene quality is obtained from each technique. From mono to multilayer and/or from µm² to large area; these properties make it suitable for many applications. For an easiest use of this material and for its characterization, the interest of transfer techniques was developed and a non-exhaustive list method was described. Finally, the impact of the transfer technique on graphene properties was reported. Indeed, according to the transfer method used, some surface modification, such as wrinkles, cracks or tears or pollution such as residues can deteriorate the graphene quality and some solution to limit or avoid these were listed.
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Challenges for the future, according with the timeline presented by Novoselov et al. [24], are to develop growth techniques of graphene on various kind of substrate in order to avoid the transfer step and/or achieve a transfer method without pollution and/or find a good cleaning process.

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