Preparation of Graphene

Selected Topics in Physics: Physics of Nanoscale Carbon

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Today there are several methods for the preparation of graphene. In the following some of these methods will be presented and discussed. They will be compared using specific requirements and allocated to different purposes. The requirements are e.g. quality and size of the flakes or controllability of the resulting coating.

1 Introduction

Graphene is a very special material, since it has the advantage of being both conducting and transparent. The transparency of a material normally depends on its electronic properties and requires a band gap. Under normal conditions transparency and conductivity exclude each other, except for a few compounds like indium tin oxide (ITO). However, in contrast to ITO, graphene is also flexible and capable of withstanding high stress. Therefore it is very attractive for the application of flexible electronic devices, e.g. touch screens [1]. Accordingly, there are a lot of efforts in order to prepare graphene easyly with the required properties.

The methods described in this review are evaluated on the bases of different requirements: On the purity of the graphene, which is defined by the lack of intrinsic defects, (*Quality*) as well as on the size of the obtained flakes or layers (*Size*). Another aspect is the amount of graphene which can be produced simultaneously (*Amount*) or the complexity such as the requirement of labour or the need for specially designed machines (*Complex.*). One last attribute is the controllability of the method in order to achieve reproducible results (*Control.*).

This review is organized as follows: In Sec. 2 the exfoliation methods are presented and discussed. Following that another type of preparation, the growth of graphene, will be introduced in Sec. 3. Concluding, the different methods will be compared in Sec. 4.

2 Exfoliation

Basically there are two different approaches to preparing graphene. On the one hand graphene can be detached from an already existing graphite crystal, the so-called exfoliation methods, on the other hand the graphene layer can be grown directly on a substrate surface. The first reported preparation of graphene was by Novoselov and Gaim in 2004 [2] by exfoliation using a simple adhesive tape.

2.1 The "Scotch Tape Method"

In this micromechanical exfoliation method, graphene is detached from a graphite crystal using adhesive tape. After peeling it off the graphite, multiple-layer graphene remains on the tape. By repeated peeling the multiple-layer graphene is cleaved into various flakes of few-layer graphene. Afterwards the tape is attached to the substrate and the glue solved, e.g. by acetone, in order to detach the tape. Finally one last peeling with an unused tape is performed.

The obtained flakes differ considerably in size and thickness, where the sizes range from nanometers to several tens of micrometers for single-layer graphene, depending on the preparation of the used wafer. Single-

layer graphene has a absorption rate of 2%, nevertheless it is possible to see it under a light microscope on SiO_2/Si, due to interference effects [3]. However, it is difficult to obtain larger amounts of graphene by this method, not even taking into account the lack of controllability. The complexity of this method is basically low, nevertheless the graphene flakes need to be found on the substrate surface, which is labour intensive. The quality of the prepared graphene is very high with almost no defects.

2.2 Dispersion of Graphite

Graphene can be prepared in liquid-phase. This allows upscaling the production, in order to obtain a much higher amount of graphene. The easiest method would be to disperse the graphite in an organic solvent with nearly the same surface energy as graphite [4]. Thereby, the energy barrier is reduced, which has to be overcome in order to detach a graphene layer from the crystal. The solution is then sonicated in an ultrasound bath for several hundreds hours or a voltage is applied [5]. After the dispersion, the solution has to be centrifuged in order to dispose of the thicker flakes.

The quality of the obtained graphene flakes is very high in accordance with the micromechanical exfoliation. Its size however is still very small, neither is the controllability given. On the other hand, the complexity is very low, and as mentioned above this method allows preparing large amounts of graphene.

2.3 Graphite Oxide Exfoliation

The principle of liquid-phase exfoliation can also be used to exfoliate graphite oxide. Due to several functional groups like epoxide or hyroxyl, graphene oxide is hydrophilic and can be solved in water by sonication or stirring. Thereby the layers become negatively charged and thus a recombination is inhibited by the electrical repulsion. After centrifugation the graphene oxide has to be re-
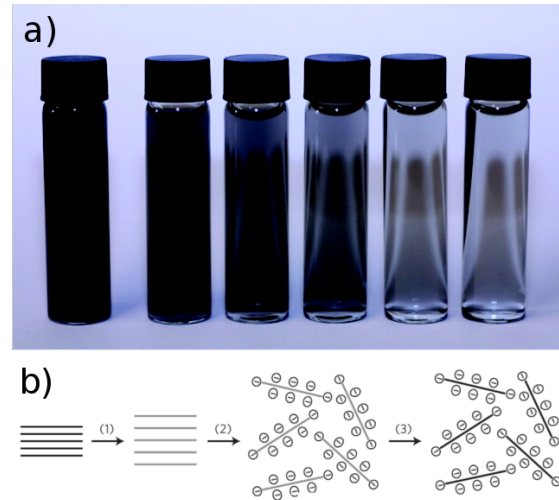

Figure 1: **(a)** Solution of graphene in liquid-phase. The flasks contain solutions after centrifugation at different frequencies [4]. **(b)** Scheme of the exfoliation of graphite oxide. The graphite gets oxidized and solved in water. Afterwards it gets reduced to graphene [6].

duced to regular graphene by thermal or chemical methods. It is hardly possible to dispose of all the oxygen. In fact, an atomic C/O ratio of about 10 still remains [6].

The performance of this method is very similar to liquid-phase exfoliation of pristine graphene. Only the complexity is higher, since graphite oxide has to be produced first, wich requires the use of several chemicals. Also the obtained graphene oxide has to be reduced afterwards, using thermal treatments or chemicals again [7]. The reduced graphene oxide is of very bad quality compared to pristine graphene, nevertheless graphene oxide could be the desired product. Graphene oxide modified with Ca and Mg ions is capable of forming very tensile graphene oxide paper, as the ions are crosslinkers between the functional groups of the graphene flakes [8].

2.4 Substrate Preparation

There are different methods for substrate preparation in order to use the dispersed graphene in a non liquid-phase. By vacuum

filtration the solution is sucked through a membrane using a vacuum pump. As a result the graphene flakes end up as filtration cake of graphene paper.

The deposition of graphene on a surface can be done by simple drop-casting where a drop of the solution is placed on top of the substrate. After the solvents have evaporated, the graphene flakes remain on the surface. In order to achive a more homogeneous coating the sample can be rotated using the spin-coating method in order to disperse the solution with the help of the centrifugal force. With spray-coating, the solution ist sprayed onto the sample, which allows the preparation of larger areas.

3 Growth on Surfaces

A totally different approach to obtaining graphene is to grow it directly on a surface. Consequently the size of the obtained layers are not dependent on the initial graphite crystal. The growth can occur in two different ways. Either the carbon already exists in the substrate or it has to be added by chemical vapour deposition (CVD).

3.1 Epitaxial Growth

Graphene can be prepared by simply heating and cooling down an SiC crystal [9]. Generally speaking single- or bi-layer graphene forms on the Si face of the crystal, whereas few-layer graphene grows on the C face [10]. The results are highly dependent on the parameters used, like temperatur, heating rate, or pressure. In fact, if temperatures and pressure are too high the growth of nanotubes instead of graphene can occur. The graphitization of SiC was discovered in 1955, but it was regarded as unwelcome side effect instead of a method of preparing graphene [11].

The Ni(111) surface has a lattice structure very similar to the one of graphene, with a missmatch of the lattice constant at about 1.3% [11]. Thus by use of the nickel diffusion method a thin Ni layer is evaporated onto a SiC crystal. Upon heating the carbon diffuses through the Ni layer and forms a graphene or graphite layer on the surface, depending on the heating rate. The thus produced graphene is easier to detach from the surface than the graphene produced by the growth on a simple SiC crystal without Ni [11].
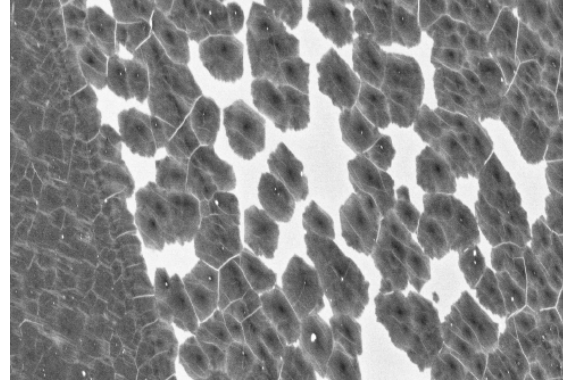

Figure 2: SEM image of graphene on copper foil. At several locations on the surface graphene islands form and grow together [14].

The growth of graphene starts at several locations on the crystal simultaneously and these graphene islands grow together, as shown in Fig. 2). Therefore the graphene is not perfectly homogeneous, due to defects or grain boundaries. Its quality therefore is not as good as that of exfoliated graphene, except the graphene would be grown on a perfect single crystal. However, the size of the homogeneous graphene layer is limited by the size of the crystal used. The possibility to produce large amounts of graphene by epitaxial growth is not as good as by liquid-phase exfoliation, though the controllability to gain reproducible results is given. Also the complexity of these methods is comparatively low.

3.2 Chemical Vapour Deposition

Chemical vapour deposition is a well known process in which a substrate is exposed to gaseous compounds. These compounds decompose on the surface in order to grow a thin film, whereas the by-products evaporate.
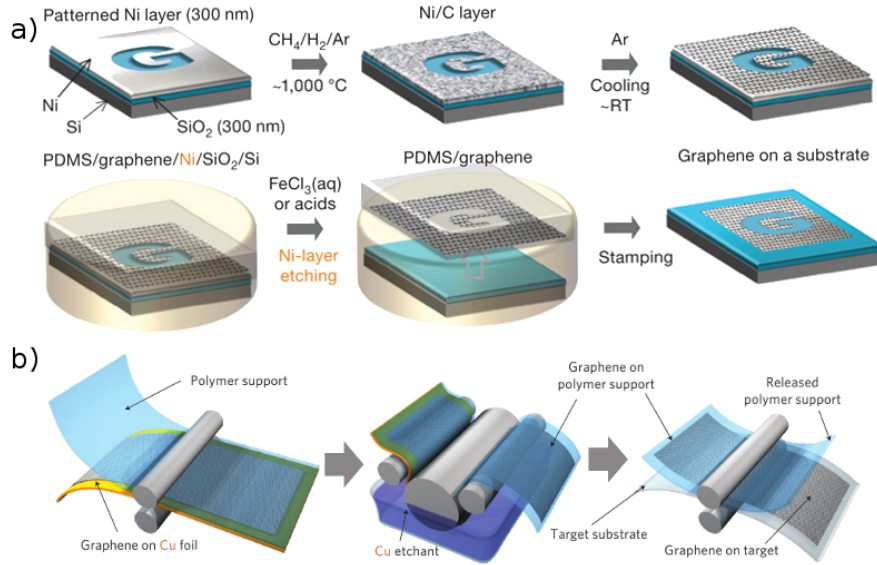
Figure 3: **(a)** Scheme of preparation of graphene by CVD and transfer via polymer support. The carbon solves into the Ni during the CVD and forms graphene on the surface after cooling. With a polymer support the graphene can be stamped onto another substrate, after etching of the Ni layer. Patterning of the Ni layer allows a control of the shape of the graphene [12]. **(b)** Roll-to-roll process of graphene films grown on copper foils and transferred on a target substrate [1].

There are a lot of different ways to achieve this, e.g. by heating the sample with a filament or with plasma. Graphene can be grown by exposing of a Ni film to a gas mixture of H_2, CH_4 and Ar at about 1000 °C [12]. The methane decomposes on the surface, so that the hydrogene evaporates. The carbon diffuses into the Ni. After cooling down in an Ar atomosphere, a graphene layer grows on the surface, a process similar to the Ni diffusion method. Hence, the average number of layers depends on the Ni thickness and can be controlled in this way. Furthermore, the shape of the graphene can also be controlled by patterning of the Ni layer.

These graphene layers can be transfered via polymer support, which will be attached onto the top of the graphene. After etching the Ni, the graphene can be stamped onto the required substrate and the polymer support gets peeled off or etched away. Using this method several layers of graphene can be stamped onto each other in order to decrease the resistance. Due to rotation relatively to the other layers, the turbostratic graphite does not have the Bernal stacking and consequently the single graphene layers hardly change their electronic properties, since they interact marginally with the other layers [1].

Using copper instead of nickel as growing substrate results in single-layer graphene with less than 5% of few-layer graphene, which do not grow larger with time [13]. This behavior is supposed to be caused due to the low solubility of carbon in Cu. For this reason *Bae* and coworkers developed a roll-to-roll production of 30-inch graphene [1]. Using CVD, a 30-inch graphene layer was grown on a copper foil and then transferred onto a PET film by a roll-to-roll process. CVD also allows a doping of the graphene, e.g. with HNO_3, in order to decrease the resistance. *Bae* and colleagues stacked four doped layer of graphene onto a PET film and thus produced a fully functional touch-screen panel. It has about 90% optical transmission and about 30 Ω per square resistance, which is superior to ITO.
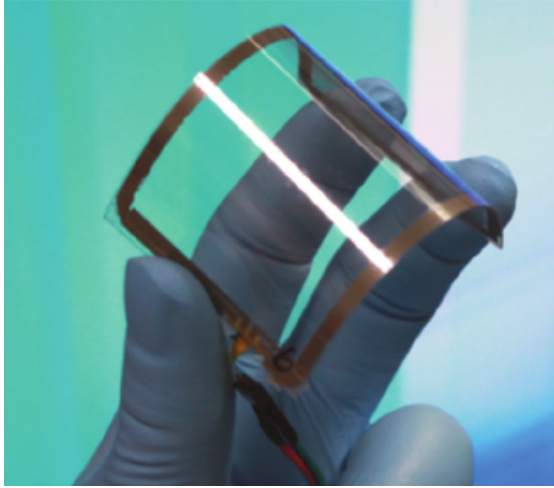
Figure 4: Assembled graphene/PET touch panel shows high mechanical flexibility [1].

Method	Quality	Size	Amount	Complex.	Control.
Adhesive Tape	✓	×	×	(✓)	×
Liquid phase	✓	×	✓	✓	×
Graphite oxide	–	×	✓	×	×
Epi. growth	×	(✓)	×	✓	✓
CVD	×	✓	✓	✓	✓

Table 1: Overview of the performances of the different methods.

The mechanical performance test showed a much higher withstanding of graphene compared to ITO. In fact, the resiliance was not limited by the graphene itself, but by the attached silver electrodes.

In conclusion the author states that the optical and electrical performance of graphene prepared by CVD is very high, but the purity, which would be necessary for laboratory research, is not given. On the other hand, the thus produced graphene layers can be very large and are easily obtained in large amounts. The complexity is rather low, since CVD is a well-known method and often used in industry. Therefore there is no need to develop new machines or techniques. Furthermore, perfect control of the results is given as well as transportability.

4 Summary

An overview of the different methods and their performances is given in Tab. 1. In summary, the exfoliation methods have the advantage of providing graphene of very high quality and purity, and, due to the low complexity, they are perfect for laboratory research. The size of the obtained flakes, however, as well as the controllability are too poor for industrial production.

On the other hand, the growth of graphene on surfaces allows a more or less unlimited size of the graphene layers and a high controllability, which makes these methods applicable for industrial production. The purity, however, is not very high, which makes these methods unsuitable for laboratory research of graphene. Since CVD is an already used method in industry, the epitaxial growth of graphene is probably a dead end technique.

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