



Review article

Mechanisms of graphene fabrication through plasma-induced layer-by-layer thinning



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ABSTRACT

Graphene is a layer of sp^2 hybridized carbon of a single-atomic thickness, which exposes most of its atoms to the surrounding medium. The properties of graphene are highly dependent on its number of layers. Currently, the synthesis of uniform graphene with a specific number of layers in a controllable way is rather hard. In this review, we present the highlights of current advances regarding utilization of various plasmas for the control of graphene thickness. The mechanisms involved in the etching phenomenon of the graphene sheet to realize the layer control are particularly analyzed and compared. A precise layer-by-layer etching could be achieved using controlled operating parameters of different kinds of plasmas applied to graphene and combined with sub-layer substrate effects. With this review, we propose a concise overview of the application of plasma as the basis of development of new approaches to obtain uniform graphene with the desired number of layers in near future.

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1. Introduction

Monolayer graphene, a thin film of carbon with honeycomb lattice and thickness of one or a few atomic layers [1], is one of the

most fascinating new materials currently created. The attractiveness of graphene, and especially monolayer graphene, is basically attributed to its astounding electronic properties [2,3], such as the occurrence of massless Dirac fermions due to the linearity of electron dispersion around the Fermi level under the smallest binding energy [4–7]. Monolayer graphene also shows an anomalous integer quantum hall effect that is seldom found in other

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materials; it is a special phenomenon that is only exhibited by certain semiconductor devices at low temperature and high magnetic field [7]. Graphene possesses extremely high charge carrier mobility due to the exceedingly narrow quantum well. The electron mobility for a free-standing monolayer graphene exceeds $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with the maximum value recorded at $230,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [8] and its electronic properties are more similar to a zero bandgap semiconductor [9]. Graphene is also known to be one of the strongest materials on earth with a Young's modulus of 1 Tpa [10], which is ~200 times stronger than steel. With a visible light transmittance up to 97% possessed by monolayer graphene, it is also known as one of the best transparent conductive materials [11].

Most of the astonishing properties of graphene highly depend on the number of layers. As the number of layers is increased, as soon as the number is above 2 layers, their properties are dramatically modified. The charge carrier of bilayer graphene shows a parabolic dispersion at low energy well described with massive Dirac fermions with a finite density of states at zero energy, similar to the conventional unrelativistic electrons [12–14]. The electronic bandgap also deviates with the number of layers of graphene [15]. Trilayer graphene possesses unique intrinsic electronic properties [16]. Furthermore, this kind of deviation is also the reason why graphene can be used in different applications depending on the number of layers it possesses.

The layer control of graphene is becoming the primary task in graphene research. There are 2 general routes investigated in the aim of controlling the layer number of graphene. First, the bottom up approach consists of a direct grow of graphene with the desired number of layer through CVD by using Cu as catalyst to grow monolayer graphene [17], or Ni usually assisted by fast cooling to limit the layer of graphene segregation [18,19] and etc. However, the control of graphene of desired layers still remains as a challenging task and requires a very precise regulation of the operating parameters. On the other hand, the top down approach utilizes various techniques to remove the excessive layers of post-synthesis graphene either by applying purely physical etching, or by combining physical and chemical etching processes [20] through plasma, ozone [21], high temperature oxidation [22], energetic irradiation by positive ions [23], protons [24] or electrons [25] and laser thinning [26]. However, most of the methods aforementioned could easily cause excessive etching and introduce unnecessary defects in the graphene basal plane. Scalability and precision manipulation of graphene layers is important to advantageously incorporate into respective devices. Among all the methods aforementioned, plasma etching is the most widely applied and the most promising approach.

Plasma is an ionized gas made up of radicals, positive ions and negative particles (electrons), in the ratio that makes the overall electric charge equal to zero. Plasma has proven its potential to be applied in vast area including chemistry, physics, engineering, biology, microbiology and medicine [27]. In the field of nanocarbons, plasma is commonly combined with Chemical Vapor Deposition (CVD) to form Plasma Enhanced Chemical Vapor Deposition (PECVD). PECVD utilizing electrical energy either by RF (AC) frequency or DC discharge between two electrodes to generate a glow discharge (plasma) in which the energy is transferred into a gas mixture. The gas mixture turns to reactive radicals, ions, neutral atoms and molecules, and other highly excited species. In the research for the CVD reaction, either on the synthesis of carbon nanotubes (CNTs) or graphene, plasma plays a crucial role in providing extra energy to enhance the formation of CNTs and graphene. In fact, the electric field in the plasma system was believed to provide an additional force inducing alignment of CNTs [28]. In conventional PECVD, the formation of high energy reactive

species in the gas phase by collision to provide energy for the nucleation of graphene and CNTs. The substrate of the sample can be maintained at a lower temperature as compared with conventional CVD process. It is very important as a polymer-based substrate or a temperature sensitive substrate is used. On the other hand, the continuous bombardment of plasma to the as-grown graphene would cause extensive damage to the basal plane. Attributed to the damaging properties of plasma on graphitic materials, researchers are searching for the possibility to open up a new top-down approach and obtain much more uniform graphene.

The production of thin layer graphite and oxidation of graphitic materials by either molecular oxygen or atomic oxygen was explored and monitored under electron microscope since half century ago [29,30]. Meanwhile, the etching ability of plasma on graphite was widely studied, either on colloidal graphite [31] or highly oriented pyrolytic graphite (HOPG) [32]. The study was started before the discovery of graphene in 2004 [2]. In that case, the etching mechanisms were studied mainly regarding their effect on the bulk graphite submitted to high intensity plasmas. Graphene which exposes most of its atoms to the surrounding medium is extremely sensitive to its environment [33] and then, it is highly sensitive to any plasma treatment. The process that consists the layer-by-layer thinning of graphene is very sophisticated and it requires high level of plasma control. Plasma is furthermore broadly utilized for the graphene edge etching in order to adapt the particular application such as electronic gate, transistor and etc.

In this review, we discuss the recent advances of the graphene thinning research using plasma and the various techniques applied to obtain graphene with a fixed number of layers and size. We describe in details the mechanisms involved in the etching of graphene or graphite with various types of plasma, in order to produce uniform graphene with a controlled thickness. The known strategy to enable precise layer-by-layer thinning of plasma is also discussed and the future prospects regarding the role of plasma etching in graphene layer control wrap up the discussion.

2. Oxygen plasma

Oxygen plasma is relatively strong among the conventionally utilized plasmas in research. Dioxygen gas is known to be a good oxidizing agent and it has a very strong affinity with carbon materials. As a result, oxygen plasma is often preferentially selected for graphene or graphite etching. Etching is a process that induces detachment of species or blocks from the solid material either through physical or chemical approaches [34]. Understanding precisely the mechanisms involved in removal of carbon atoms by oxygen plasma is especially important for graphene thinning processes; sensitivity of the etching process has to be thus controlled at the atomic scale. Simulations were used to deeply investigate and identify the elements or species involved in graphene etching since several decades. Some articles use the word “graphite single layer” rather than graphene, and some of the reports were published before the discovery of Geim and Novoselov [2]. Majority of the simulations using graphene model that very tiny in scale and composed with tens to hundreds carbon atoms in their study; they normally name this material as “thin layer graphite”, since the name “graphene” was not widely known at that period.

2.1. Epoxide formation on graphene

Ions, radicals, electrons and photons are the major components of plasma. Etching of graphenic carbon by plasma could be accomplished by mainly 2 routes. (1) Physical plasma etching is provoked by a continuous bombardment of ions accelerated by a potential gradient. (2) Chemical process is completed by the

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