Graphene Etching: How Could it be Etched?

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Abstract: Background: A new nanomaterial species called “graphene” has been of great interest owing to its outstanding mechanical, thermal, chemistry, and physical characteristics. The etching either directly from chemical vapor deposition growth process or plasma technology process has been emerging as attracting research topic in achieving the thinner graphene layer and cleaner surface in order to improve their electronics and optoelectronics. The resided impurities and the high roughness surface are because of the nature of graphenes induced in deteriorating the performance. Removal of the impurities by surface cleaning or plasma-related graphene etching through the layer-by-layer thinning method as a top-down lithography. In particular, new plasma-based graphene etching is free-damage while maintaining its $\pi$-binding, which affects its conductivity.

Objective: This mini-review will address the latest progress related to graphene etching technology based on emerging strategies. From here, it might be adopted in the etching of other nanomaterials.

Keywords: Atomic layer etching (ALE), chemical vapor deposition (CVD), graphene etching, inductively coupled plasma (ICP), ion beam, neutral beam, plasma, reactive ion etching (RIE).

1. INTRODUCTION

Through the mechanical graphite exfoliation utilizing the scotch tape in 2004 [1, 2], an ultrathin graphene layer has discovered and emerged as the most promising nano-sized material with the amazing electronic properties [1-19]. Unfortunately, the conductive graphene with gapless characteristics limited its novel physical and chemical properties. Therefore, the tuning of band-gap of graphene by using various strategies related to chemistry, physic, nanotechnology, and engineering for layer-by-layer removal or contaminant removal is highly demand in superior performance device applications (Fig. 1).

To do this, the etching technology shows the great ability and gets the interests of the scientists and researchers in academy and industry through the world [20-29]. Several new methods have found out (i) plasma (inductively coupled plasma (ICP)), neutral beam assisted atomic layer etching (ALE), ion beam ICP, the reactive ion etching (RIE)) [20-27], (ii) the chemical vapor deposition (CVD) [28], or (iii) thermally activated Fe nanoparticles [29]. Plasma technology has been used to etch fine features in Si integrated circuits in the last four decades [20]. Among breakthroughs that were required to make this possible, plasma etching plays an important role for the silicon and nonsilicon (metal)-based devices. In this mini-review, the role and the progress of the etching technology processes on graphene using new innovation etching approaches, and the related-applications will be presented.

2. GRAPHENE ETCHING: HOW COULD IT BE ETCHED?

Different layer numbers of graphene have different band-gap value, for instance, the single layer has no band-gap, but bilayer has a band gap which can be used to make a transistor with higher on/off current ratio. The etching of graphene via layer-by-layer strategy will make: (i) the cleaner graphene surface with removed contaminants and residues, (ii) thinner graphene film leading to less and band-gap value until no bang-gap at single graphene layer. There are the uncountable amount of applications which needs ideally free-defect single-layer graphene or free-defect multilayer graphene film and no need for the appearance of band-gap such as a flexible display, touch panel, solar cell, fuel cell, etc. Depending on the types of defects such as disorder [30], doping [31], external field [32], mechanical strain [33-37] etc, it could be contributing to host material (e.g. graphene) as useful (increase the conductivity, mobility, work function) or harmful (decrease the conductivity, mobility, work function) [38]. As the result, the band-gap value could be an increase or decrease depending on the types of vacancy defects [38].

The plasma etching showed the great advantages, for instance, easily to scale-up as well as manipulation, and mass
Fig. (1). Schematic of etching of graphene few-layers or nanoribbon on arbitrary substrate surfaces through plasma, nanotechnology, physics, chemistry, and engineering in tuning their electronics.

Fig. (2). (a) Schematic of the graphene etching process by O₂ plasma. (b) Schematic of two possible etching mechanisms of ground electrode oxygen plasma: anisotropic vertical and horizontal etchings. Water-droplet contact angle measurement of graphene/SiC before (c) and after (d) O₂ plasma etch. (e) On-chip device based on oxygen-etched nanosphere graphene. (a, b) are reproduced with permission from [21], copyright 2014, Springer. (c, d) are reproduced with permission from [22], copyright 2010, American Chemical Society. (e) is reproduced with permission from [23], copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
production. By applying the O\textsubscript{2} plasma, the graphene multilayers were well etched on different substrates such as SiO\textsubscript{2} [21, 23], or SiC [22]. In 2014, Al-Mumen \textit{et al.} reported the singular sheet etching from bilayer graphene using O\textsubscript{2}, the grounded electrode ICP and RIE systems regarding the various plasma etching directions (vertical and horizontal) (Fig. 2a,b) [21]. However, this method introduced a few defects, but the defects occurred much less if treated by the ICP compared than the RIE due to the higher energy damage from the RIE. Raman data also provided the proof through the disorder characteristics based on the I\textsubscript{D}/I\textsubscript{G} ratio which are 0.94 and 1.18 when using the RIE and ICP, respectively [21]. Treating on another substrate, SiC, the water-droplet contact angle result changed from 92.7\(^{\circ}\) (multilayer), 91.9\(^{\circ}\) (bilayer), 92.5\(^{\circ}\) (single layer) down to 70\(^{\circ}\) when one layer etched away at the conditions of 10 W and 2 min of epitaxial graphene (Fig. 2c,d) [22]. In another report, by nanosphere lithography using low-power O\textsubscript{2} plasma etching, Liu \textit{et al} showed that the etched ordering of graphene nanoribbons (GNRs) on SiO\textsubscript{2} was well performed in many shapes including branches, chains, connected rings, and circular rings (Fig. 2e) [23].

Another method in combination of plasma treatment and post-anneling for layer-by-layer thinned-etching, Yang \textit{et al.} utilized the N\textsubscript{2} plasma and post-anneling (Ar/O\textsubscript{2} mixture in 900\(^{\circ}\)C). As a result, this dry-etch method thinned regarding layer-by-layer facilely from the intrinsic multilayer graphene (Fig. 3a-c) [24]. In a recent breakthrough, the etching method was showed by Lim \textit{et al.} [25] and Kim \textit{et al.} [26]. Lim \textit{et al.} utilized a neutral beam assisted ALE for a two-step process of O\textsubscript{2} radical absorption and desorption Ar neutral beam irradiation (Fig. 3d). Consequently, the multilayer graphene was etched with each single layer of graphene. Although, this plasma etching method is much better than the previous report [22-25], however, the defects still occur slightly on the graphene network as the D peak of Raman
spectra in this report [25]. In the latest report, Kim et al. innovated by inserting the double mesh grid between the plasma source and the substrate holder in a plasma system (Fig. 3c-j) [26]. By this etching strategy, the damage on graphene surface almost did not occur during a two-step plasma etching process using the O$_2$ radical chemical absorption and desorption Ar physical ion beam irradiation in ICP system with the controlled-plasma energy at lowering of 11.2 eV.

In addition, there are still strategies in previous reports on the etching treatment of graphene surface such as plasma etching by Ar/H$_2$ mixture in RIE (Fig. 4a) [27], or H$_2$ etching during CVD graphene growth (Fig. 4b-e) [28], or thermally activated Fe nanoparticles (Fig. 4f, g) [29]. The demonstrated results showed high defects with high D band in Raman spectra [27], or the random and non-uniform nanoribbon-etched graphene film [28], or the random- and non-uniform-etched graphene nanotrenches [29]. As compared to the above existing methodologies developed for etching, the etching strategy in Kim et al. [26] showed the most superior to date owing to the free-damage and perfectly layer-by-layer thinned etching on multilayer graphene film during the plasma etching from this innovative ion beam ICP system.

For device applications related to the etched-graphene studies above as shown in Table 1, a chip device based on nanosphere-etched GNRs by low-power O$_2$ plasma has been carried out [23], and showed the superior electronic quality device as well as achieved the expected GNRs architectures (chains, branches, circular rings). A transistor has fabricated as a metal-oxide-semiconductor (MOS), unfortunately, the etching effect of graphene was obtained but simultaneously the high energy plasma damage also occurred resulting in the poor electrical characteristics [25]. The fabrication of the monolayer-deep pattern based on the etched graphene by N$_2$ plasma and annealing in Ar/O$_2$, Yang et al. showed this pattern in rather good quality with a few defects [24]. The fabrication of Y- and Z-shaped GNRs during the graphene CVD growth process, the etching effect strongly occurred through a high H$_2$ concentration [28]. However, the results of Y- and Z-shaped GNRs were still randomly and not yet well-controlled mechanically.

**CONCLUSION AND FUTURE OUTLOOK**

Generally, there are many unexploited huge potentials from the etched-graphene products, but the perspectives on
Table 1. A classification of graphene etching strategies and the related-applications. Here, “NA” means “not applicable”.

<table>
<thead>
<tr>
<th>Etching Strategies</th>
<th>Substrate</th>
<th>Applications of Etched-Graphene</th>
<th>Results</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanosphere lithography using low-power O$_2$ plasma etching</td>
<td>SiO$_2$</td>
<td>Chip device based on nanosphere-shaped graphene nanoribbons (GNRs)</td>
<td>Superior electronic quality and achieved GNRs architectures included chains, branches, circular rings, and connected rings at low cost</td>
<td>[23]</td>
</tr>
<tr>
<td>O$_2$ plasma etching</td>
<td>SiC</td>
<td>NA</td>
<td>NA</td>
<td>[22]</td>
</tr>
<tr>
<td>O$_2$ plasma etching by ICP-RIE</td>
<td>SiO$_2$</td>
<td>NA</td>
<td>NA</td>
<td>[21]</td>
</tr>
<tr>
<td>N$_2$ plasma + Post annealing (Ar/O$_2$)</td>
<td>SiO$_2$</td>
<td>Monolayer-deep patterns</td>
<td>Thinned graphene with good quality with few defects</td>
<td>[24]</td>
</tr>
<tr>
<td>O$_2$ absorption + Ar etching by neutral beam</td>
<td>SiO$_2$</td>
<td>Metal-oxide semiconductor (MOS) devices</td>
<td>Poor electrical characteristic due to high energy damage</td>
<td>[25]</td>
</tr>
<tr>
<td>O$_2$ absorption + Ar etching by ion beam</td>
<td>SiO$_2$</td>
<td>NA</td>
<td>NA</td>
<td>[26]</td>
</tr>
<tr>
<td>Reactive ion etching (RIE) system using Ar/H$_2$ mixture</td>
<td>SiO$_2$</td>
<td>NA</td>
<td>NA</td>
<td>[27]</td>
</tr>
<tr>
<td>H$_2$ etching during CVD graphene growth</td>
<td>Cu foil</td>
<td>Y- and Z-shaped GNRs</td>
<td>Obtained Y- and Z-shapes with controlled-H$_2$ etch process</td>
<td>[28]</td>
</tr>
<tr>
<td>Thermally activated Fe nanoparticles</td>
<td>SiO$_2$</td>
<td>NA</td>
<td>NA</td>
<td>[29]</td>
</tr>
</tbody>
</table>

that would be bright. If these etching methodologies are applied to the other low-dimensional materials such as transition metal dichalcogenides (TMDs) or transition metal carbides, nitrides, and carbonitrides (MXenes), surely that, it could unlock a new chapter for high-quality electronics and optoelectronics. The increasing of controlled band-gap of 2D materials will do much improvements of the current on-off ratio, photoluminescence, and other unexplored exotic properties. The layer-by-layer thinned etching of other 2D materials by low-energy plasma technology (free-damage ICP, neutral beam, ion beam) with extremely less inducing the physical and chemical damage will be next interesting research direction, in particular, it has been systematically demonstrated on graphene etching [26].

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The author declares no conflict of interest, financial or otherwise.

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REFERENCES
