Chapter

The New Etching Technologies of Graphene Surfaces

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Abstract

Recently, graphene nanomaterial has drawn great interest due to its excellent electrical and optoelectrical properties. The etching of graphene based on plasma engineering to achieve atomically thin layer and extremely clean surface is a hot issue, which is highly desirable for industrial applications. The resided contaminants with high intrinsic roughness create the degradation of performance. The impurities are removed via surface cleaning method and layer-by-layer plasma etching via top-down lithography. Recently, new plasma technology-based etching causes no damage and secures its π-binding, which plays a key role in conductivity and other characteristics. Thus, this chapter presents the recent advances in new etching technologies for nanomaterials (e.g., graphene) as well as emerging applications based on these technologies.

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

1. Introduction

An atomical graphene layer, which was invented in 2004 [1, 2], is considered as one of the best candidates for a broad application range with novel electronic and optoelectronic behaviors [1–21]. Unfortunately, the conductive graphene with no bandgap prevented its outstanding physical and chemical potentials. Thus, its bandgap tuning via various approaches is highly desired for extreme performance devices (**Figure 1**).

Recently, etching technologies are emerging as one of the best efficient tools to tune a device's performance, thereby extending to many different fields in broadband [20–30]. The new approaches include the following: (i) inductively coupled plasma (ICP), neutral beam-based atomic layer etching (ALE), ion beam and reactive ion etching (RIE) [22–29], (ii) chemical vapor deposition (CVD) [30, 31] and (iii) thermally activated nanoparticles [32]. Plasma has used Si-integrated circuits for etching [22]. Among breakthroughs, plasma etching represents an important role in Si and non-Si (metal)-assisted devices. This chapter will present recent advances in new graphene etch technologies and their related applications.

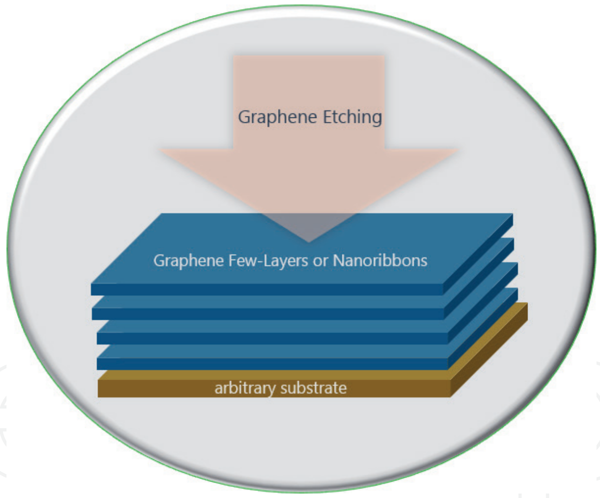

Figure 1.
Etch processing of graphene few-layer or graphene nanoribbon on various substrates through plasma, physic, chemistry to tune its electronics and optoelectronics.

2. Emerging etch technologies of graphene surfaces

Graphene layers have a number of independent bandgaps, e.g., single layer has no bandgap, but a bilayer has bandgap, and could be utilized to make transistor a superior performance. The layer-by-layer graphene etching would form (i) a cleaner surface with removed residues and (ii) thinner graphene film leading to smaller bandgap value until there is no bandgap at a single layer. Depending on the types of defects such as disorder [33], doping [34], external field [35] and mechanic strain [36–40], the etching can make the host material (e.g., graphene) very useful (high conductivity, high mobility, high work function, etc.) [41]. As a result, bandgap can be higher (or lower) depending on the types of vacancy defects and etching rates [41].

2.1 O_2 plasma etching

Plasma etch technology presents many advantages such as easy scale-up, manipulation and mass production. Under O_2 plasma exposure, graphene multi-layers were well-etched on SiO_2 [23, 25] or SiC [24]. In 2014, the etching of host bilayer graphene was carried out by O_2 using ICP and RIE apparatuses on the vertical and horizontal etch directions (**Figure 2a, b**) [23]. However, this approach formed defects during the use of RIE, but the defects were very few in the ICP case because of the high damage energy of RIE. Raman data provided the proof through disorder characteristics based on I_D/I_G ratio (0.94 and 1.18) when utilizing RIE and ICP, respectively [23]. Treating another substrate, SiC, the contact angle changed from 92.7° (multilayer), 91.9° (bilayer) and 92.5° (single layer) down to 70° when one layer epitaxial graphene etched away at 10 W and 2 min (**Figure 2c, d**) [24]. In 2011, through nanosphere lithography with low-power O_2 plasma, Liu et al. found out the etched ordering of graphene nanoribbons (GNRs) on SiO_2, which performed well in various shapes such as branches, chains, connected rings and circular rings (**Figure 2e**) [25].

2.2 N_2 plasma etching and postannealing

Yang et al. utilized N_2 plasma and postannealing (Ar/O_2, 900°C), another technology in integration of layer-by-layer thinned plasma and post-annealing.

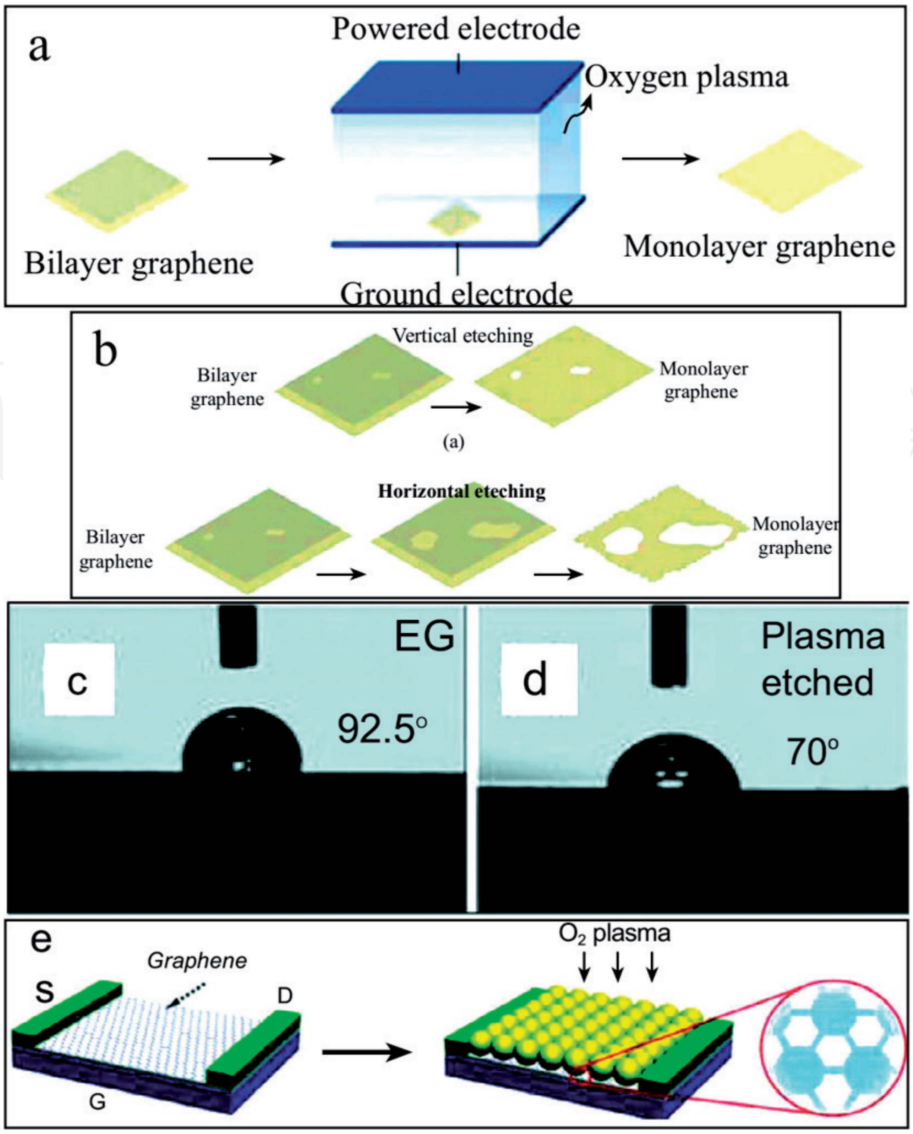

Figure 2.
(a) Sequence of graphene etching via O_2 plasma. (b) Schematic of two etching mechanisms of O_2 plasma: vertical etching and horizontal etching. (c, d) The contact angle of graphene/SiC without/with O_2 plasma, respectively. (e) On-chip device assisted by O_2-etched nanosphere graphene ((a) and (b) are reproduced with permission from [23], Copyright 2014, Springer; (c) and (d) are reproduced with permission from [24], Copyright 2010, American Chemical Society; (e) is reproduced with permission from [25], Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

As a result, this dry-etching thinned regarding layer-by-layer easily from intrinsic multilayer graphene (**Figure 3a**–**c**) [26]. In another innovative etch technology by Lim et al. [27] and Kim et al. [28], Lim et al. utilized a neutral beam ALE via two-step process of O_2 radical absorption and Ar neutral beam desorption, and multilayer graphene was well-etched for each layer (**Figure 3d**). Although this etching was much more effective than the previous study [24–27], defects formed slightly on graphene lattice as high Raman D-peak (**Figure 3c**) [27].

2.3 Cyclic etching (O_2 adsorption and Ar desorption by ion beam)

In 2017, Kim et al. newly innovated by adding two mesh grids between the plasma source and the substrate holder in the ICP chamber (**Figure 3e**–**j**) [28]. Consequently, the damage on graphene surface disappeared after the two-step plasma etching process of chemical absorption of O_2 radical and physical desorption of Ar ion beam at optimized plasma energy (11.2 eV).

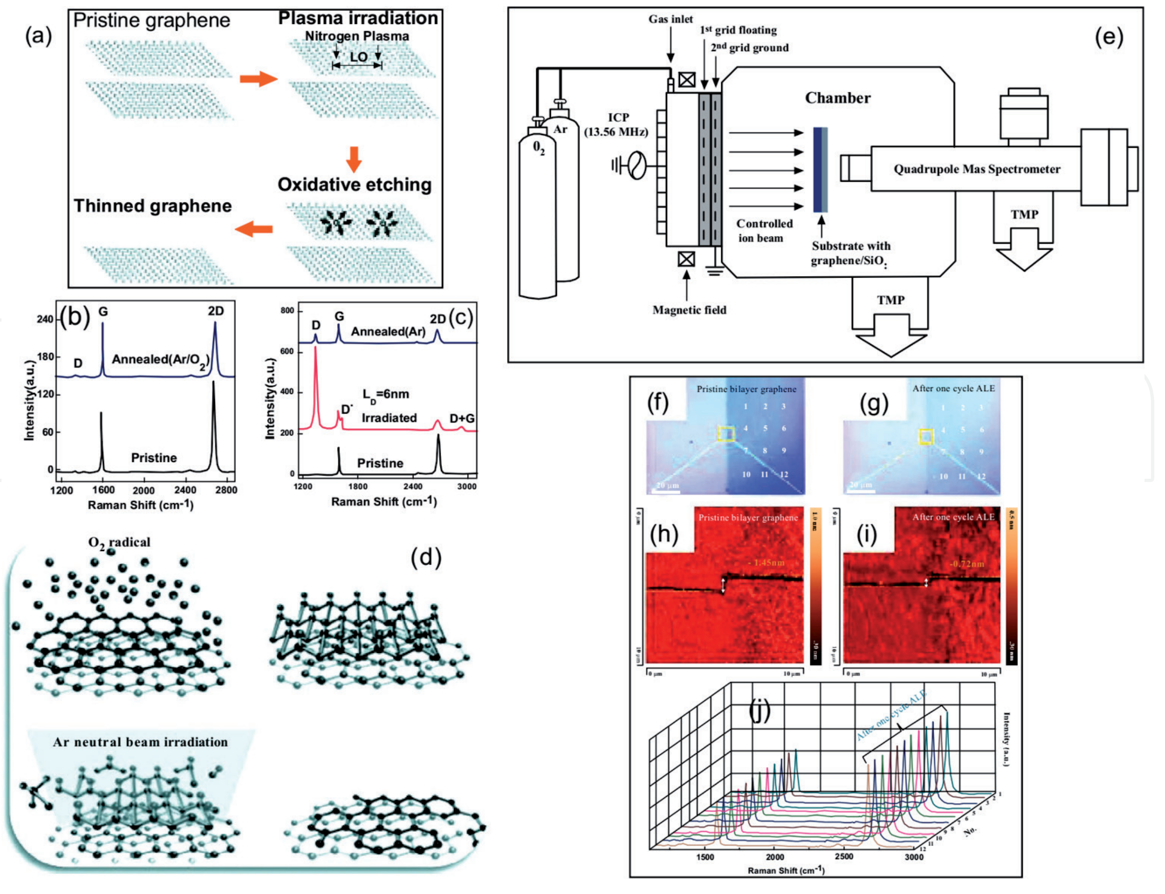

Figure 3.
(a) Sequence of layer-by-layer etching via N_2 irradiative and oxidative etch. (b, c) Raman data of pristine, irradiated and annealed multilayer graphene. (d) Schematic of ALE process of graphene via O_2 radical absorption and Ar neutral beam desorption. (e) A double-grid ICP ion beam apparatus for graphene etching via chemical O_2 absorption and physical low-energy Ar ion beam desorption. (f, g) OM and (h, i) AFM data of pristine bilayer graphene, and after an ALE cycle. (j) Raman data of pristine bilayer graphene after an ALE cycle for white dots of (f, g) ((a–c) are reproduced with permission from [26], Copyright 2011, IOP Publishing; (d) is reproduced with permission from [27], Copyright 2012, Elsevier; (e–j) are reproduced with permission from [28], Copyright 2017, Nature Publishing Group).

2.4 Others (RIE, H_2, CH_4/H_2 and Fe NPs)

In addition, there are still strategies for graphene surface etching such as Ar/H_2 mixture in reactive ion etching (RIE) (**Figure 4a**) [29], H_2 etching during CVD graphene growth (**Figure 4b–e**) [30], CH_4/H_2 etching during CVD graphene growth (**Figure 4f**) [31] or thermally activated Fe nanoparticles (NPs) (**Figure 4g, h**) [32]. However, the demonstrated results showed high defects through very high D-peak intensity in Raman spectra [29] or the random and nonuniform nanoribbon-etched graphene [28] and nanotrench-etched graphene based on Fe NPs [32]. Compared with the developed etch technologies above, the etching method by Kim et al. [28] revealed to be the best to date because of perfectly no damage and layer-by-layer etching from an innovative ion beam ICP.

3. Applications based on etched graphene

In **Table 1**, applications associated with the above etched-graphene investigations are briefly summarized. A chip utilized nanosphere-etched GNRs by O_2 plasma at low power [25] and revealed the high-performance electronic device

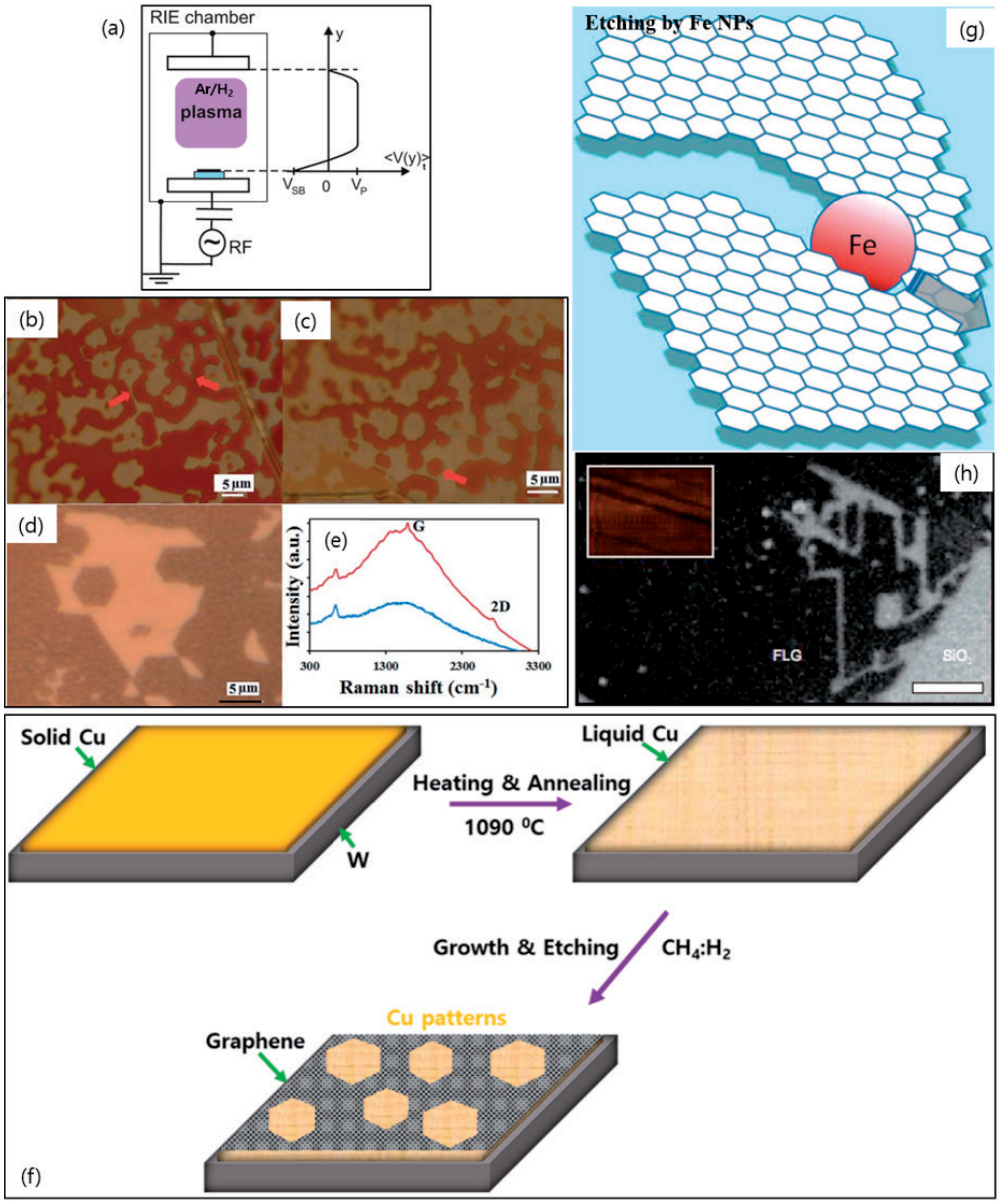

Figure 4.
(a) An RIE apparatus using Ar/H₂ to etch graphene on SiO₂. OM data of H₂-etched graphene during CVD growth and then annealing (Ar/H₂, 1000°C) under ambient atmosphere (b–d). (e) Raman data of etched graphene and partially oxidized Cu surface. (f) Schematic of few-layer graphene etching by thermally activated iron nanoparticles. (g) SEM data of etched few-layer graphene as nanotrench; tiny dots are iron NPs; scale bar is 0.8 μm. Inset is AFM data of few-layer graphene after being etched ((a) is reproduced with permission from [29], Copyright 2011, AIP Publishing; (b–e) are reproduced with permission from [30], Copyright 2015, the Royal Society of Chemistry; (f) is reproduced with permission from [31], Copyright 2018, American Chemical Society; (g) and (h) are reproduced with permission from [32], Copyright 2008, American Chemical Society).

with the exotic GNR architectures (chain, branch and circle ring). In another application, a metal oxide semiconductor (MOS)-like transistor was made; although the etched effect was formed, it simultaneously produced a high-energy plasma damage that induced poor electrical characteristics [27]. One more application related to the monolayer deep patterning was fabricated by etching (N_2) and annealing (Ar/O_2), and this pattern presented good quality for slight defects [26]. In 2015, Papon et al. fabricated the Y- and Z-shaped GNRs during CVD graphene growth, and the etching effect vehemently happened at high H_2 concentrations [30]. But these shapes were random and not well-controlled mechanically.

Etching methods	Substrate	Applications of Etched- Graphene	Results	Ref.
Nanosphere lithography using low-power O_2 plasma etching	SiO_2	Chip device based on Nanosphere-shaped graphene nanoribbons (GNRs)	Superior electronic quality, and achieved GNRs architectures included chains, branches, circular rings, and connected rings at low cost	[25]
O_2 plasma etching	SiC	NA	NA	[24]
O_2 plasma etching by ICP-RIE	SiO_2	NA	NA	[23]
N_2 plasma + post annealing (Ar/O_2)	SiO_2	Monolayer-deep patterns	Thinned graphene with good quality with few defects	[26]
O_2 absorption + Ar etching by neutral beam	SiO_2	Metal-oxide semiconductor (MOS) devices	Poor electrical characteristic due to high energy damage	[27]
O_2 absorption + Ar etching by ion beam	SiO_2	NA	The best atomically layer-by-layer etching candidate to date	[28]
Reactive ion etching (RIE) system using Ar/H_2 mixture	SiO_2	NA	NA	[29]
H_2 etching during CVD graphene growth	Solid Cu foil	Y- and Z-shaped GNRs	Obtained Y- and Z-shapes with controlled-H_2 etch process	[30]
CH_4/H_2 etching during CVD graphene growth	Liquid Cu foil	NA	Obtained hexagon flower shape with integrated growth/etch process	[31]
Fe nanoparticles	SiO_2	NA	NA	[32]

Table 1.
Graphene etching methods and their applications. Source: "NA" is "not applicable".

4. Conclusions

Generally, there are many unexploited huge potentials from the etched-graphene products, but the perspectives are bright. If these etching technologies are extended to other nanomaterials such as transition metal dichalcogenides (TMDs) or transition metal carbides, nitrides, and carbonitrides (MXenes), and black phosphorous [42], it will definitely achieve high-quality electronics and optoelectronics. Bandgap tuning for nanomaterials will significantly improve the on/off current ratio, photoresponsivity, quantum efficiency, conductivity and others. Layer-by-layer etching for multilayer materials by low-energy plasma technology (double mesh grids inserted for plasma apparatus such as chlorine-radical ICP, neutral-beam ICP and ion beam ICP) with no physical damage would be the next research direction and can be applied to the other low-dimensional materials [28, 43] to achieve ultrahigh performance of electronic and optoelectronic devices [28, 43]. For instance, in the latest report in 2019, Kim et al. utilized a chlorine ICP innovative plasma apparatus that has no physical damage effect by inserting double mesh grids for cyclic ALE process on intrinsic multilayer MoS_2 and successfully fabricated heterostructured photodetector with ultra-responsivity (~10^6 A/W) in the visible range [43].

Conflict of interest

There are no conflicts of interest to declare.

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