

Ultra-fine fabrication of Graphene by Hydrogen Plasma Etching

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[Summary]

There are high expectations that atomically thin graphene sheets will be a key material for reducing the size of electronic devices and sensors. Although the ratio of the edge area to the whole sample increases as the size of the device is reduced, current graphene fabrication techniques have difficulty in controlling edge structures in atomic scale, and therefore, there is concern about the effect of random electronic states on the overall properties of devices due to nonuniform edge structures. Our research is focused on developing hydrogen plasma etching (HPE) technique, which can create a zigzag edge selectively, as a versatile method for forming graphene in desired structures with atomically ordered edges. This article introduces atomic scale fabrication (ultra-fine fabrication) of graphene using a combination of HPE and existing nanofabrication techniques and discusses graphene edge structures created using HPE.

1 Introduction

Graphene is a mono-atomic sheet of carbon atoms with a thickness of 0.34 nm. Since it was successfully manufactured for the first time in 2005¹⁾, its superior electrical and mechanical properties became clear, and research was developed in a wide range of fields, targeting not only the miniaturization and the high integration of existing electronic devices but also next-generation sensors and devices using the inherent properties of graphene. Strictly speaking, the name “graphene” exclusively means a monolayer one, but several or tens of stacked layers are often called graphene as well. Research of multilayer graphene is also flourishing especially in application point of view because it has properties not observed in monolayer graphene. The basic properties and possible applications of graphene were introduced in the previous issue of Anritsu Technical²⁾.

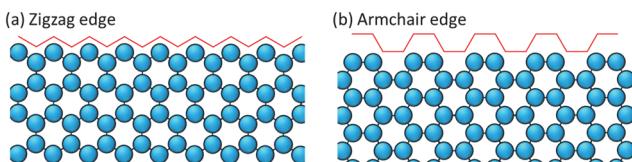


Figure 1 Schematic pictures of graphene edges. Blue spheres represent single carbon atoms.

(a) Zigzag edge. (b) Armchair edge.

This article focuses on the edge properties of graphene, which are especially important among other graphene properties. Since carbon atoms in graphene are bound to form a honeycomb lattice, the edge takes one of two forms: a zigzag edge, or an armchair edge (Figure 1). The armchair edge has

the same properties as the graphene interior (bulk), but the zigzag edge shows a characteristic electronic state not appeared in the graphene bulk^{3), 4)}. For nano-scale graphene ribbons having zigzag edges on both sides (zigzag Graphene Nano-Ribbon: z-GNR), the electron spin (magnetic properties of each electron) is expected to be polarized along edges³⁾. Due to this state, z-GNR is expected to be a hopeful material for “spintronics” devices that transfer data using electron spin rather than charge, and therefore, consume ideally no electric power.

While graphene has big potential, various technical problems must be solved before it is used in actual devices. Incorporating graphene into devices will require processing into various shapes. The Oxygen-Plasma Etching (OPE) of graphene to remove unwanted parts as well as the mechanical cut using a very sharp tip are rather popular for the fabrication of graphene. These techniques can process graphene with nanometer-scale accuracy into any shape. However, they cannot control the edge structure in atomic scale (about 0.1 nm). If an edge structure is not uniform, and the edges have a random mixture of zigzag and armchair with totally different electronic states, the edge electronic state cannot be controlled, making it impossible to fabricate stably operable nanoscale devices. Since miniaturization of electronic devices, etc., down to the nanometer-scale, where the role of the edge in the entire device becomes important, is expected to continue in the future, further manufacturing to nanometer-scale using conventional methods will be limited. As a

spintronic device, for instance, where an edge itself carries a spin flow (power supplier), the fabrication of a z-GNR with atomically precise zigzag edges is inevitable.

One method to obtain an atomically uniform edge structure is a bottom-up approach to build graphene by polymerization of molecules containing benzene rings which are building blocks of the graphene lattice structure⁵⁾, but this method has a strong limitation on the shape of the sample because it is based on the specific chemical reaction. In this manner, there is a tradeoff between achieving freedom in the sample shape and an atomically uniform edge structure as far as using these conventional methods.

We have focused on Hydrogen-Plasma Etching (HPE) technique for solving this difficulty. Our previous article²⁾ introduced a method for creating nanoscale hexagonal holes (hexagonal nanopits) with a zigzag edge by exposing graphene to hydrogen plasma at high temperatures. If the hexagonal nanopit position and size can be controlled, one can expect to shape graphene with ideal zigzag edges by placing the hexagonal nanopits with desired size at desired positions.

This article is organized as follows. The first part of this article describes the challenges in nanoscale fabrication of graphene and the suitability of HPE for this. The second part outlines the HPE technique and our trial fabrication of graphene using this technique. The last part introduces some evaluations of the edge formed by HPE using Atomic Force Microscopy (AFM)⁶⁾ and laser Raman spectroscopy⁷⁾.

2 Hydrogen Plasma Etching (HPE)

2.1 Graphene HPE

Plasma etching technique is used widely for nanoscale processing in the semiconductor industry, etc. The following is a simple explanation of the basic principle. A high frequency electromagnetic field is applied to the etching gas to break the molecular bonds and form a plasma composed of highly reactive atoms (radicals) and ions. The combination of the radicals and ions with atoms at the substrate surface produces highly volatile compounds that separate from the surface. Repeating this reaction over causes progressive surface etching. Regions where etching is not required are protected by a coating with chemicals such as resists to finally produce a required surface structure. Since the reactivity and volatility of the reaction products is determined by the

combination of the gas species and substrate material, it is important to choose the appropriate gas species. This facilitates selective etching of the substrate surface. Let us take graphene exfoliated on the surface of SiO₂ substrates as an example. Oxygen plasma which is often used to clean SiO₂ substrate only etches the graphene and does not etch the substrate, while CHF₃ plasma etches both the graphene and the SiO₂ substrate. Like oxygen plasma, hydrogen plasma only etches the graphene without any effect on the SiO₂ substrate. This etching is known to proceed in two steps: First, defects are created on the graphene surface, and second, these defects are enlarged anisotropically to form hexagonal nanopits (anisotropic etching). Using HPE alone produces randomly distributed defects but another preprocessing method can be used to form defects as nucleation centers of the hexagonal nanopits at specified locations, offering high expectations for fabrication of graphene into desired structure with zigzag edges.

Although the reaction between hydrogen plasma and either graphene or graphite (stacked graphene) is generally represented as $4\text{H} + \text{C} \rightarrow \text{CH}_4$ (gas) and etching advances with the release of methane, the actual reaction is thought to be more complex. For example, there is a theoretical consideration⁸⁾ that CH₃ is generated from the surface. The reason why zigzag edges are selectively produced and nanopits are shaped into hexagons is qualitatively understood that the armchair edges have higher reactivity, which leaves the residual less-reactive zigzag edges. However, the details are still being researched.

The mechanism of HPE has also been studied experimentally by measuring dependences of etching parameters such as the positional relation with the plasma glow⁹⁾, the reaction temperature (T)^{10), 11)}, the gas pressure (P)⁹⁾, the RF power of the plasma generator (W_{RF})¹⁰⁾, and the reaction time (t)¹⁰⁾. A study on graphite HPE reported⁹⁾ that, as the distance between the sample and the plasma glow increases, the etching results change from a large number of small nanopits with circular shapes to a small number of large hexagonal nanopits⁹⁾. Hydrogen plasma contains hydrogen (H) radicals composed of a single atom with an unpaired electron as well as positively charged H ions (H⁺, H₂⁺, and H₃⁺), and H radicals are more conserved than H ions far from the plasma center. Since the plasma glow is thought to be caused

by the H ions, there is a suggestion that the H ions form the initial defects and then H radicals expand the defects into the hexagonal nanopits.

The etching temperature is quite an important etching-reaction parameter. Previous research^{10), 11)} reported most active etching at $T = 400$ to 500°C . This is explained qualitatively as follows. At low temperatures when $T < 200^\circ\text{C}$, the H ions and H radicals have insufficient thermal energy to bond with the carbon atoms, but at high temperature when $T > 700^\circ\text{C}$, the C-H bond is formed but immediately broken without occurring etching reactions because of too high thermal energy. Therefore, effective etching only occurs in a limited temperature window. However, different research groups have reported different details about temperature dependency. While Ref.[10] reported that the etching rate changes continuously with temperature to form a smooth peak, Ref.[11] reported that the peak shape changes discontinuously at about 450°C . These results means that attention is required because the HPE reactivity itself depends highly on the etching environment.

It is important to correctly understand the characteristics in each experimental setup, because the etching behavior changes according to the positional dependency between the plasma glow and the sample position, and the temperature dependencies are different in each setup. We have investigated the characteristics of our HPE system using graphite which is qualitatively expected to produce the same etching results as graphene. The detail of our HPE equipment is described in our previous article²⁾.

2.2 Reaction Position Dependency

Since the distribution of H radicals and ions in the plasma can depend not only on the distance from the glow center but also on the distance from the walls in the etching chamber, we investigated etching differences at the bottom and center parts of the etching chamber. Figures 2(a) and (b) show Scanning Tunnelling Microscope (STM) images of graphite surfaces etched at the center and bottom part of the etching chamber, respectively. As shown clearly by the STM images, the sample at the center of the etching chamber (Figure 2(a)) has many nanopits with circular shape in contrast to the sample from the bottom of the chamber (Figure 2(b)) with fewer and larger hexagonal nanopits. We believe that the density of H ions at the bottom of the chamber is lower

because electron is transferred from the wall of the chamber to the ions. This is consistent with the dependency on the distance from the plasma glow to the sample reported previously⁹⁾. Since we want to strengthen nanopit expansion while suppressing defect formation effect in this research, subsequent HPE tests were performed at the bottom of the chamber.

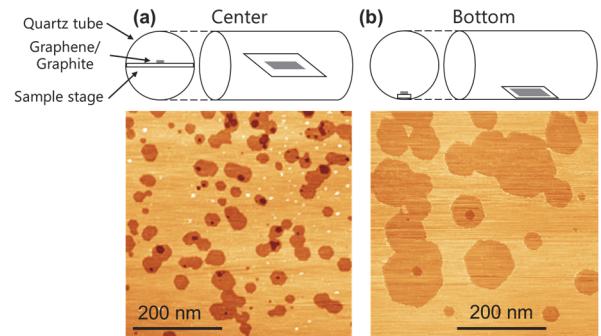


Figure 2 STM images of graphite surfaces after HPE at two locations in the etching chamber ($T = 600^\circ\text{C}$, $P = 1.5 \times 10^2 \text{ Pa}$, $W_{\text{RF}} = 25 \text{ W}$, $t = 5 \text{ min}$).
(a) Bottom. (b) Center.

2.3 HPE Temperature Dependency

Figures 3(a) to (e) are STM images of graphene surfaces processed by HPE at different temperatures $T = 300$ to 700°C . The results show the severest etching was at $T = 500^\circ\text{C}$, while there was suppressed etching at $T = 300^\circ\text{C}$ and 700°C , which matches previous studies qualitatively.

Here, we define two indices as shown in Figure 3(f) for evaluating etching behavior. One is the surface ratio S_n (area fraction of the n-th layer from the top), and the other is D_{\max} (maximum diameter of nanopits on the first layer). Although we cannot distinguish whether the surface structure has a lot of small nanopits or a few big ones using S_n only, the difference can be distinguished using D_{\max} to evaluate defect formation and hole expansion separately. Figures 3(g) and (h) show the temperature dependency of S_n and D_{\max} , respectively. Figure 3(g) shows the severest etching occurs at $T = 400$ to 500°C and etching becomes gradually less with increasing or decreasing temperature, while Figure 3(h) clearly shows that D_{\max} changes between 400°C and 500°C suddenly. This indicates that the many small nanopits are formed at $T = 400^\circ\text{C}$ and the few large nanopits are formed at $T = 500^\circ\text{C}$, which can actually be seen in Figures 3(b) and (c). The cause of this discontinuous change is unknown but qualitatively matches the observations in Ref.[10]. From

here on, our research fabricated hexagonal nanopits with the zigzag edge by HPE at $T = 600^\circ\text{C}$.

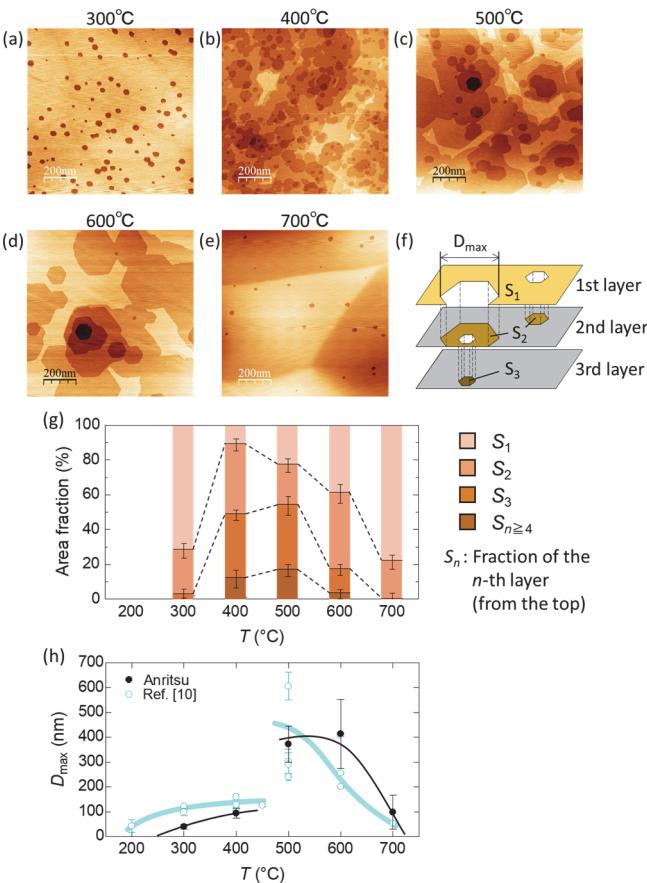


Figure 3 (a) to (e) STM images of graphite surfaces after HPE at $T = 300$ to 700°C ($P = 1.5 \times 10^2 \text{ Pa}$, $W_{\text{RF}} = 20 \text{ W}$, $t = 5 \text{ min}$). (f) Definition of surface ratio S_n and the maximum diameter of nanopits D_{\max} . (g) Temperature dependency of S_n . (h) Temperature dependency of D_{\max} . The solid lines are the guide-to-the-eyes.

2.4 Edge Structure Evaluation using HREELS

The ideal zigzag edge which is expected to realize spin polarization must not only has an atomically uniform structure but also maintain the same crystal structure as the bulk, called the sp^2 bonding. Although, as described in the previous article²⁾, the atomically uniform edge structure is confirmed by measuring the electronic state using STM¹²⁾, whether the edge is sp^2 or sp^3 bonding has not been confirmed experimentally. Thus, we investigated it using High Resolution Electron Energy Loss Spectroscopy (HREELS). The HREELS measures the molecular and lattice vibration at the surface. By measuring the vibration energy of the C-H bond, one can evaluate whether the edge is terminated by hydrogen as well as whether the edge is sp^2 bonded or not.

Although the details are omitted here, this measurement has confirmed the sp^2 bonding at the edge created by HPE. Based on these results, the zigzag edge shaped by HPE is revealed to maintain the sp^2 bonding as well as an atomically uniform structure.

3 Graphene Ultra-fine fabrication and Edge Structure

3.1 Graphene Ultra-fine fabrication

We now understand the HPE parameter dependency of our equipment from the experiments presented in the previous section. As the next step, we are testing atomic scale fabrication of graphene using HPE (called ultra-fine fabrication in this article).

So far, Ultra-fine fabrication of graphene using HPE was reported by Shi *et al.*¹³⁾ They used electron beam lithography and OPE technique to create defects in the graphene that are then enlarged into hexagonal nanopits using HPE¹³⁾. However, this was reported by just one research group and we have been unable to reproduce the same result in our setup. If the anisotropic etching can start from a defect, etching should progress from the flake edge as well, but we have been unable to confirm anisotropic etching starting from the flake edge. These facts suggest that not all defects become the nucleation centers for hexagonal nanopit formation. In this research, instead of using OPE, CHF_3 plasma is used to prepare holes through to the SiO_2 substrate, which is then followed by HPE (Figure 4(a)).

Figure 4(b) shows an AFM image immediately after creating holes on multi-layer graphene (about 6 layers) and Figure 4(c) shows the hexagonal nanopits after subsequent HPE. In Figure 4(b), graphene exists in only the upper half of the image, in which there is a white (high) region surrounding the black (deep) hole. The lower half of the image is the SiO_2 substrate without graphene and there are no white regions. These results indicate that graphene swells around the holes. On the other hand, Figure 4(c) shows that the graphene, the brightest part, is shaped by HPE and the pre-patterned holes are enlarged into hexagonal nanopits. Since HPE etches graphene selectively, there is no change to the shape of the holes in the SiO_2 substrate.

In this way, we succeeded in arranging hexagonal nanopits by using CHF_3 plasma to create defects that act as

nucleation centers. Since size of the hexagonal nanopits depends only on the reaction time (t) by fixing the other parameters such as the sample position in the chamber, the reaction temperature (T), the hydrogen gas pressure (P), and the RF power (W_{RF}), this method can be used to create hexagonal nanopits of the desired size at the desired position.

The process has high degrees of freedom in design by controlling not only the position but also the shape of the pre-patterned hole. When positioning two oval holes parallelly along the zigzag crystallographic direction, as shown in Figure 5, HPE shapes them into elongated hexagonal nanopits. Since the edges of these hexagonal nanopits is a zigzag structure, a z-GNR is obtained in the region sandwiched between the nanopits. In Figure 5, multi-layer graphene was ultra-fine fabricated to successfully create a z-GNR with a width of 80 nm and a length of 1 μm .

As described previously, the zigzag edge created by HPE is expected to have both an atomically uniform structure and sp^2 bonding. However, these are based on the studies on the hexagonal nanopits created spontaneously on the graphite surface rather than graphene. Therefore, we used AFM⁶⁾ and laser Raman spectroscopy⁷⁾ to evaluate the graphene edges obtained by this ultra-fine fabrication technique.

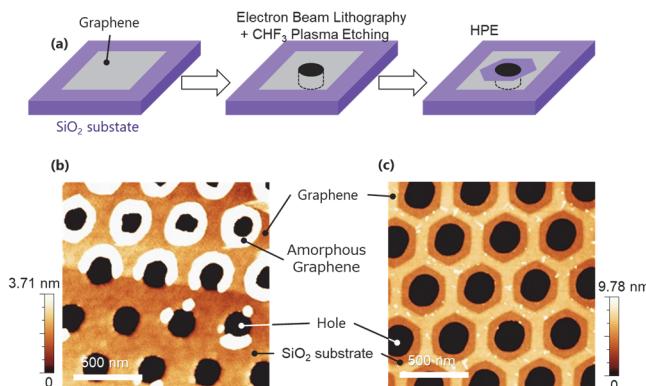


Figure 4 (a) Schematic pictures explaining the ultra-fine fabrication. Holes through to SiO_2 substrate are opened first and are enlarged into hexagonal nanopits by HPE. (b) AFM image immediately after opening hole in 6-layer graphene. (c) AFM image after HPE ($P = 1.5 \times 10^2 \text{ Pa}$, $W_{RF} = 20 \text{ W}$, $t = 1 \text{ min.}$); the same graphene flake as is shown in (b) but the image is obtained at different position.

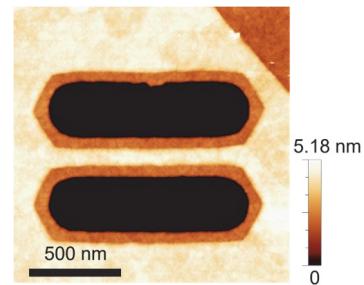


Figure 5 AFM image of graphene with oval holes after HPE ($P = 1.5 \times 10^2 \text{ Pa}$, $W_{RF} = 20 \text{ W}$, $t = 1.5 \text{ min.}$). Hexagonal nanopits became elongated according to the hole shape. Between nanopits, z-GNR with a length of about 1 μm and width of about 80 nm is obtained.

3.2 Raman Spectroscopy

Raman spectroscopy is a method of investigating the molecular vibration and lattice vibration which are specific to materials by measuring the energy shift of scattered light from the incident light. As well as identifying the material, it is used to measure crystal orientation, surface stress, etc. We used a laser with a wavelength of 532 nm for this measurement.

Figure 6 shows the typical Raman spectra for mono-, bi- and multi-layer graphene. The Raman spectra of graphene and graphite have peaks around 1350 cm^{-1} , 1600 cm^{-1} , and 2650 cm^{-1} called the D, G, and 2D-bands, respectively. The G-band originates from the honeycomb structure composed of sp^2 -bonded carbon atoms. Since the intensity I_G is proportional to the area of the part with graphene-type structure in the measured region, the spectra shown hereafter are normalized by I_G in order to compare their intensities with each other. The 2D-band is due to the second order lattice vibration, and the ratio with I_G and the peak shape are often used to identify the number of layers because the 2D-band has strong dependency on the number of layers. As shown in Figure 6, the 2D-band of monolayer graphene can be fitted to a single Lorentzian function and the intensity I_{2D} is larger than I_G , while the peak shape changes to the combination of multiple Lorentzian peaks and I_{2D} becomes smaller than I_G as the number of layers increases. The D-band is caused by a certain scattering process called inter-valley scattering and is used to evaluate the defect density in the graphene because it appears when there are defects in the honeycomb structure. However, it should be noted here that inter-valley scattering does not occur at the zigzag edge, even though the zigzag edge is also a kind of defects. Consequently, the D-band appears at the graphene armchair edge and the edge

with random atomic structure, while it does not appear at the atomically uniform zigzag edge.

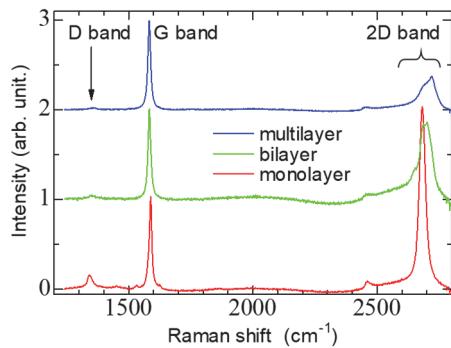


Figure 6 Raman spectra of mono-, bi-, and multi-layer graphene. The intensities are normalized by I_G . The origin for bi- and multi-layer graphene is offset.

3.3 Edge Structure of Ultra-fine fabricated Graphene

Figure 7 shows the AFM images and the Raman spectra of the graphene samples processed by different fabrication techniques, namely, graphene shaped by OPE (Figure 7(a) to (d)), graphene with holes created by CHF_3 plasma (Figure 7(e) to (h)), and graphene with hexagonal nanopits shaped by HPE (Figure 7(i) to (l)).

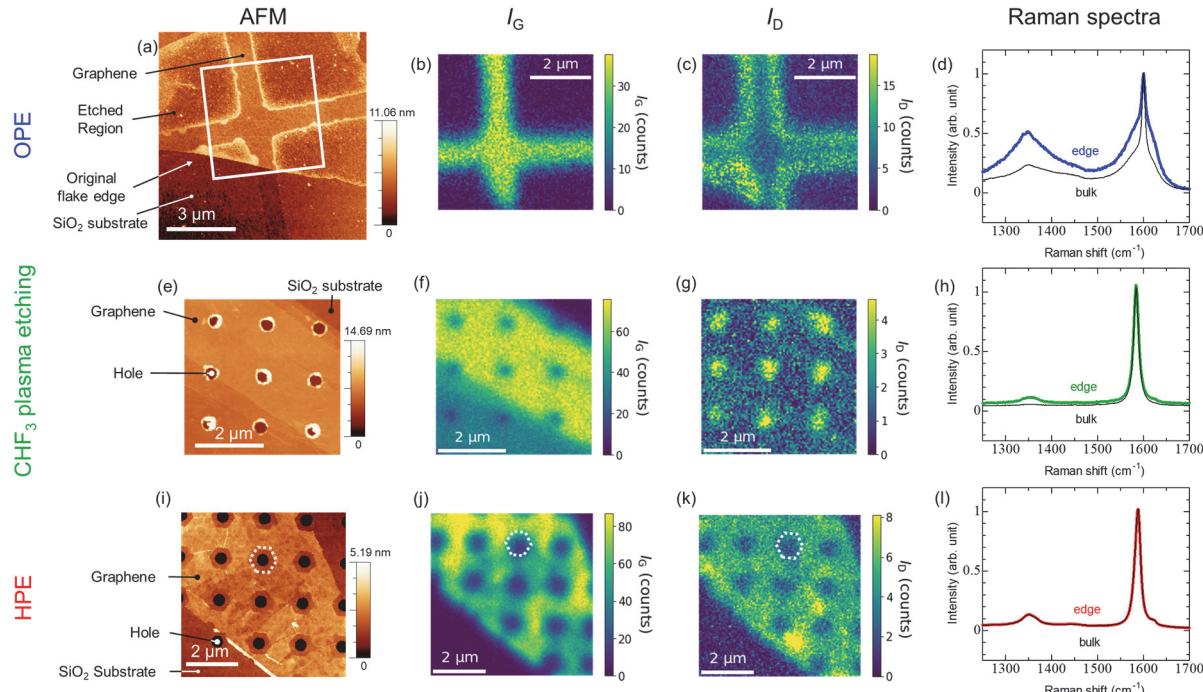


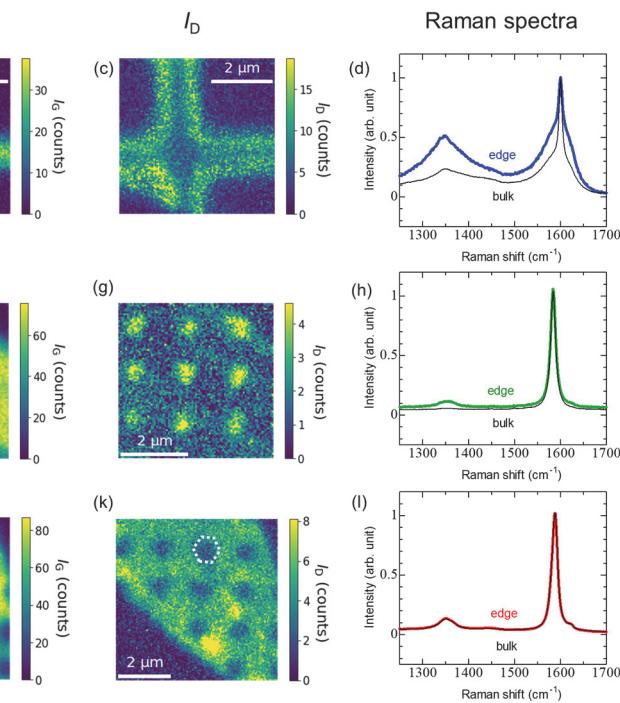
Figure 7 The results of AFM and Raman spectroscopy of graphene shaped by OPE (a) to (d), CHF_3 plasma etching (e) to (h), and HPE (i) to (l) at $P = 1.5 \times 10^2$ Pa, $W_{\text{RF}} = 20$ W, $t = 5$ min.

(a), (e), and (i) are AFM images; (b), (f), and (j) are spatial distributions of G-band intensity I_G ; (c), (g), and (k) are those of D-band intensity I_D ; (d), (h), and (l) are Raman spectra around the D and G-band, respectively. The solid black and colored lines are averaged spectra for the bulk and edges, respectively. (b) and (c) are measurements in the white frame in (a). For the other samples, AFM images and Raman spectra are measurements in the same region. The dotted white lines in (i) to (k) show the positions of hexagonal nanopits.

The AFM image of graphene shaped by OPE (Figure 7(a)) shows that the edge is covered with a swell by about 1.5 nm over about 200 nm wide. Figures 7(b) and (c) are the I_G and I_D spatial distributions, respectively, for the white frame in Figure 7(a), revealing that I_G follows the sample shape while I_D becomes stronger at the edge. In fact, the averaged Raman spectra for the sample edge and bulk (Figure 7(d)) show enhancement of the D-band at the edge, indicating that the swollen part at the edge is not a uniform zigzag edge.

As shown in Figure 7(h), CHF_3 plasma-etched sample has very few defects judging from the absence of D-band in the bulk, while a D-band is observed at the hole edges, and the AFM image (Figure 7(e)) indicates that the hole edge is covered with a swelling of 10 nm over 100 nm wide. Figures 7(f) and (g) showing the spatial distribution of I_G and I_D , respectively, indicate that I_D is enhanced at the edge. These features qualitatively match graphene shaped by OPE and suggest that the edge is not a zigzag structure.

To the contrary, for the graphene shaped by HPE, the spectrum at the edge is almost identical to that at the bulk with



no enhancement in D-band. In fact, as is clear from the AFM image in Figure 7(i), the flat structure of the graphene continues to the very edge without swelling, and I_G and I_D have the same spatial distribution (Figure 7(j) and (k)). This indicates that the edge is the uniform zigzag edge preserving graphene structure. Although a small D-band peak in the bulk (Figure 7(l)) indicates some defects created by HPE, the defects are much fewer than the sample shaped by OPE judging from sufficiently small intensity of the D-band.

4 Summary

It is heavily important for the designing of nanoscale devices to create an edge with an atomically precise structure and uniform electronic state. To this end, this research is focused on HPE technique to shape graphene with atomic precision. Since HPE can create a zigzag edge, there are high expectations for its application utilizing its unique local electronic states.

However, the mechanism of anisotropic etching of graphene using H plasma is not well understood, and the dependency of etching parameters depends on research groups. Therefore, the first stage in our research was to determine the optimum etching parameters for the HPE system constructed in Anritsu by measuring the dependency on the sample position in the chamber and reaction temperature. In addition, we investigated the crystal structure of the edge shaped by HPE, which remained unknown, using HREELS, and found that the zigzag edge shaped by HPE has not only an atomically uniform structure but also the sp^2 bonding which is the same structure as the bulk.

It is important for ultra-fine fabrication of graphene how to create defects which act as the nucleation centers of hexagonal nanopits. In our research, we successfully prepare the nucleation centers of the hexagonal nanopits subsequently shaped by HPE using CHF_3 plasma. The measurements using AFM and laser Raman spectroscopy revealed that the graphene shaped by HPE maintain flatness and crystal structure (defect density) down to the very edge.

Consequently, we established the novel ultra-fine fabrication technique by which graphene can be shaped into a desired shape with atomically uniform zigzag edges. These results are important not only to obtain better performance of graphene devices by suppressing the uncontrollable effect of

inconsistent edges but also to develop novel devices which utilize the inherent electronic states of zigzag edges.

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