Two-step method for growth of adlayer-free large-area monolayer graphene on Cu foil

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Abstract

Chemical vapor deposition is the most promising approach for synthesis of large-area monolayer graphene on Cu foil. However, numerous factors can result in formation of adlayers, such as the morphology of the Cu foil, methane concentration, and growth temperature. Here, we report atmospheric pressure chemical vapor deposition growth of large-area adlayer-free monolayer graphene by the two-step ‘bottom-up-etching’ method. The experimental results showed that a temperature increase in the second step can dramatically accelerate etching of the bottom graphene layer. A growth model for adlayer-free monolayer graphene on Cu foil is proposed.

1. Introduction

Chemical vapor deposition (CVD) is the most promising method for growing large-area graphene film on transition-metal substrates, such as copper and nickel [1–4]. The Growth of large-area single-crystal graphene and number control of the graphene layers are the two main challenges for CVD graphene growth. Cu foil is used for growth of monolayer graphene owing to the limited solubility of carbon in the Cu substrate [5]. However, adlayer (bilayer or multilayer) regions are always observed in ordinary one-step CVD graphene growth on a polycrystalline Cu substrate [1, 6–8]. Researchers have found that adlayer growth starts owing to trapping of carbon resources between the Cu substrate and graphene layer, the adlayer forms at the same initial nucleation centers, and growth terminates simultaneously with that of the first layer [2].

To enhance the uniformity of the graphene layer, the surface morphology, cleanliness and crystal orientation of the substrate, and growth conditions (temperature, pressure, and H2/CH4 ratio) have been investigated [9–14]. It has been reported that the density of the adlayers is correlated with the surface roughness of the Cu foil. Different pretreatment methods have been used to smooth the Cu-foil surface to reduce the adlayers, such as electrochemical polishing (ECP) [15–21] and chemical etching [22, 23], and to reduce carbon residues, such as high-temperature annealing [24–26]. Optimization of the H2/CH4 ratio at different stages can also realize adlayer-free growth through selective etching of the bottom multilayer graphene, which is called the ‘bottom-up-etching’ method, and the duration is 2.5–3.5 h [27]. However, these methods are either time-consuming or expensive, as shown in table 1.

Here, we report a two-step bottom-up-etching method for synthesis of adlayer-free monolayer graphene by controlling the methane concentration and temperature in different stages. In this method, we have improved growth parameters, which lead to fast etching rate of the bottom layer and less growth time compared to previous works. This study gives new insights to growth of monolayer on Cu foil substrate.

2. Materials and methods

2.1. Graphene growth

The CVD system contained a 150-mm-diameter quartz tube. The thickness and purity of the Cu foil used for graphene growth were 25 μm and 99.8%, respectively. Before growth, the Cu foil was smoothened by ECP and...
annealed at 1000 °C under 100 sccm H₂ and 1000 sccm Ar for 30 min. Graphene growth was performed at atmospheric pressure. In brief, Cu foil was placed on a quartz plate. For the one-step growth method, when the temperature reached 1000 °C with flow of 1000 sccm Ar and 50 sccm H₂, 30 sccm diluted methane (0.5% CH₄ and 99.5% Ar) was introduced into the furnace for 30 min.

For the two-step growth method, the first step was the same as the one-step method. When the first step was completed, the temperature was increased from 1000 to 1020, 1050, or 1070 °C in 5 min. For the second step, the flow rate of CH₄ was reduced to 5 sccm, and the duration was approximately 60–120 min.

2.2. Graphene transfer
After graphene growth, the graphene samples were transferred from copper to 300 nm SiO₂/Si substrates by traditional wet-transfer methods. First, a solution of polymeric methyl methacrylate (PMMA, 4% in anisole) was spin-coated on the Cu-foil surface at a speed of 2500 rpm for 40 s, followed by heating at 100 °C for 10 min. The PMMA/graphene/Cu samples were then placed in ammonium persulfate ((NH₄)₂S₂O₈) solution. After the Cu foil was completely etched, the PMMA/graphene sample was washed with deionized water and transferred onto a SiO₂/Si substrate. Finally, PMMA was removed with acetone.

2.3. Sample characterization
The morphology of graphene was characterized by optical microscopy (DM 2700M, Leica, Wetzlar, Germany) and scanning electron microscopy (SEM, Zeiss SUPER-55, Oberkochen, Germany). The quality and layer number of graphene were characterized by Raman spectroscopy (Alpha 300R, WITec, Ulm, Germany).
3. Results and discussion

A schematic of the two-step CVD process is shown in figure 1. We used a hot-wall CVD system, and a quartz plate was used to support the Cu foil, as shown in figure 1(a). The process consisted of continuous graphene-film growth with adlayers (step 1) and selective etching of the bottom multilayer (step 2) (figure 1(b)). The second step was performed at 5 sccm CH4, compared with 30 sccm CH4 in step 1, while the concentration of H2 was kept constant. A relatively high temperature (1020, 1050, or 1070 °C) was used in the second step. For comparison, we also performed experiments without a temperature change in the second step (red dashed line in figure 1(b)).

The results of the traditional one-step growth method are shown in figure 2. A SEM image of the graphene film clearly showed contrast, indicating that the film did not have constant thickness (figure 2(a)). The dark areas were uniformly distributed and corresponded to adlayer domains (figure 2(a)). An optical image of the graphene film transferred onto SiO2/Si (figure 2(b)) showed a similar phenomenon to that in figure 2(a). Raman spectroscopy is usually used to estimate the thickness and quality of graphene. The Raman spectra of the points on the graphene film marked in figure 2(b) are shown in figure 2(c). The peaks of the G band and 2D band were observed at ~1580 and ~2680 cm⁻¹, respectively. The Raman spectra results of the monolayer (blue), bilayer (red), and multilayer (black) regions were consistent with the graphene layer numbers shown in the SEM and optical images. It is clear that adlayers are a common phenomenon in one-step graphene growth on Cu foil. Beside, we have compared the morphology of Cu foils before and after graphene growth, as shown in figures 2(d) and 2(e). The root-mean-square roughness is about 14.5 nm (2d) and 5.43 nm (2e). The AFM results show that Cu foil keep flat and intergrity after long time and high temperature treatment.
The bottom-up-etching method is achieved by changing the methane concentration in different stages. On this basis, we designed a new two-step bottom-up-etching method by changing both the methane concentration and temperature in the second step. During the first growth step, the conditions of a relatively high CH\textsubscript{4} concentration and a relatively low growth temperature were used to grow a continuous graphene film with adlayers on a Cu substrate. In the second step, the temperature was increased and the CH\textsubscript{4} flow rate was decreased to a certain value at which the bottom multilayer can be selectively etched while the upper single layer can be preserved.

A photograph of the as-grown graphene/Cu sample (\~19 cm × 10 cm) is shown in figure 3(a). For this sample, we chose four locations (black rectangles in figure 3(a)) to transfer samples of the graphene film onto SiO\textsubscript{2}/Si substrates. The size of transferred films is \~5 cm × \~5 cm, as shown in the inset of figure 3(a). The samples showed a uniform color contrast, indicating that they were monolayer graphene films (figures 3(b)–(e)). Some particles and PMMA residues may have existed on these samples. The Raman spectra of the graphene film at the points marked in figures 3(b)–(e) are shown in figures 3(f)–(i), respectively. The ratios of the intensity of the 2D peak to that of the G peak were larger than 1, which means that the graphene film was a monolayer. In addition, the D band at 1350 cm\textsuperscript{-1} was hardly detected, which indicates that the uniform monolayer graphene film was high quality. These results showed that we successfully fabricated large-area adlayer-free monolayer graphene on Cu foil.

To compare the differences of the graphene films grown with and without a temperature change in the second step, a series of comparative experiments was performed with different growth temperatures and growth times, and the results are shown in figure 4. Images of the as-grown graphene film without a temperature change in the second step are shown in figures 4(a) and (b). As the growth time increased, the occupation areas of the graphene adlayer decreased. However, it was difficult to obtain an adlayer-free monolayer graphene film even when the growth time was extended to 3 h in the second step (figure 4(b)). For comparison, the results of graphene films grown with a temperature change in the second step are shown in figures 4(c)–(h). The etching phenomenon in figures 4(c)–(h) is similar to that in figures 4(a) and (b), in addition to the etching rate. For a
second-step temperature of 1020 °C, two different contrasts can be clearly observed (figure 4 (c)), which means that the multilayer graphene was removed. In contrast, when the second-step temperature was the same as that in the first step, three different contrasts can be clearly observed (figure 4 (a)). Moreover, the etching phenomenon occurred in the adlayer region, while the top layer remained a complete continuous film, indicating that selective bottom-layer etching occurred. When the growth time was increased to 180 min in the second step (figure 4 (d)), small pieces of adlayer residues were still found. When the growth temperature of the second step was increased to 1050 °C (figures 4 (e) and (f)), less adlayers were found for a duration of 60 min, and adlayer-free monolayer graphene was obtained for a duration of 90 min, which was twice as fast as for graphene growth without a temperature change in the second step. However, when the temperature of the second step was increased to 1070 °C, the etching phenomenon and etching rate were similar to those for a second-step temperature of 1050 °C, indicating that the etching rate reached the peak at 1050 °C. The results shown in figure 4 strongly support bottom-up etching and show that the temperature plays an important role in etching of the adlayer. When the temperature was increased in the second step, the etching rate of the adlayers was faster than that without a temperature change in the second step.

To elucidate the mechanism of multilayer graphene transformation to monolayer graphene, schematic illustrations of the different stages of the etching process are shown in figures 5 (a)–(c). The process can be
divided into two parts: (i) continuous graphene-film growth (figures 5(a) and (d)) and (ii) the etching stage (figures 5(b), (c) and (e), (f)). As shown in figure 5(a), during graphene growth, most of the carbon atoms diffuse to the Cu surface and form a continuous film owing to the low solubility of carbon in Cu. However, if few carbon atoms are trapped in the interface between the as-grown graphene and Cu, adlayers will form. Once a continuous graphene film is formed and the concentration of CH$_4$ is reduced, the top graphene layer has sufficient C sources to maintain its integrity, while the bottom graphene layer has insufficient carbon atoms. Furthermore, the H atoms diffuse into the graphene–Cu interface much easier than CH$_x$ radicals [27]. Combining these two factors, it is easy to understand the occurrence of bottom-up etching with the reduction of C sources and etching of H atoms, as shown in figures 5(b), (c) and (e), (f). The 2D peak intensity map in figure 5(g) shows a single layer and a bilayer corresponding to the stages in figures 5(b) and (e), which further verifies bottom-up etching. Figure 5(h) shows the 2D Raman map corresponding to the stages in figures 5(c) and (f). The consistent color confirms that a uniform monolayer-graphene film without adlayers was successfully prepared. In addition, as the temperature in the second step increased, the capability of H$_2$ etching was enhanced. It is worthy noted that H$_2$ etching of graphene strongly relies on catalytic ability of Cu. Thus, the etch starts from bottom layer contacted with Cu substrate and the etching rates are various from different Cu lattice plane. Besides, appearance of adlayer etching further confirm that H atoms diffuse into the interface much easier than CH$_4$. All of these factors led to selective bottom-up etching with an outstanding etching rate. Moreover, because a continuous graphene film with adlayers formed in the first step, less attention needs to be paid to the factors that affect formation of adlayers, such as the Cu-foil roughness, nucleation density, and CH$_4$ concentration.

4. Conclusions

Large-area adlayer-free monolayer graphene has been synthesized on Cu foil by a two-step bottom-up-etching method via atmospheric pressure CVD. Changing the CH$_4$ concentration at different stages is the key factor for

Figure 5. (a)–(c) Schematic illustrations of the etching process at different stages for preparation of monolayer graphene. (d)–(f) SEM images of the graphene film at the stages corresponding to (a)–(c). (g) and (h) Two-dimensional Raman intensity map corresponding to stages (e) and (f). Graphene-growth conditions for (d)–(f): 1000 °C, 30 sccm CH$_4$, 50 sccm H$_2$, 30 min (step one); 1050 °C, 5 sccm CH$_4$, 50 sccm H$_2$, 0, 60, and 90 min (step two).
fabrication of monolayer graphene. Reducing the CH4 concentration in the second step leads to selective bottom-layer etching because of the lack of C sources and diffusion of H atoms between the graphene–Cu interface. Increasing the temperature in the second step contributes to accelerate the etching rate owing to enhancement of the H2–etching ability. In this method, the growth time can be reduced by at least two times compared with that without a temperature change in the second step.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of Interest

The authors declare no conflict of interest.

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