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# Fabrication of single-crystal few-layer graphene domains on copper by modified low-pressure chemical vapor deposition

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A modified low-pressure chemical vapor deposition method was proposed to fabricate large-grain singlecrystal few-layer graphene domains with distinctive layers by introducing an assembly to the conventional chemical vapor deposition. It was found that the fabricated single-crystal few-layer graphene domains consist of one- to five-layer graphene areas, exhibiting layer growth characteristic. Moreover, the first three layers grew by Bernal stacking while the fourth and fifth layers could take on Bernal stacking or turbostratic stacking depending on the magnitude of the stress at the nucleation site. The results implied that the formation of few-layer graphene of good quality were beneficial from the modified low-pressure chemical vapor deposition system because not only could the assembly help provide a stable growth condition for the graphene, but it could also accelerate the generation of gaseous activated vapor carbon atoms, which guaranteed the nucleation and growth of few-layer graphene. Furthermore, the growth mechanism of the few-layer graphene was analysed.

### 1 Introduction

Graphene is a monolayer graphite with sp<sup>2</sup>-hybridized carbon atoms bonded in a two-dimensional honeycomb lattice.<sup>1,2</sup> Because of the extraordinary physical properties, such as high room temperature carrier mobility (as high as 200 000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>), long-range ballistic transport (in the magnitude of submicrometre) and high room temperature conductivity (up to 5 000 Wm<sup>-1</sup>K<sup>-1</sup>), graphene has become one of the most promising electronic materials in the post-silicon electronics.<sup>3-6</sup> Since it was firstly exfoliated from highly oriented pyrolytic graphite (HOPG) in 2004, graphene has aroused great interest of researchers.

Presently, chemical vapor deposition (CVD) on Cu is frequently used to fabricate graphene.<sup>7-12</sup> Ruoff R. S. et al. firstly synthesized polycrystalline graphene films by lowpressure CVD (LPCVD) in 2009.<sup>7</sup> Through optimizing the growth process of LPCVD, they fabricated ~0.5 mm and ~2 mm single-layer single-crystal graphene on Cu.<sup>8,9</sup> Yan Z. et al. fabricated single-layer graphene domains in millimetre by controlled chamber pressure CVD (108 Torr).<sup>10</sup> Wang H. et al. and Wu T. et al. also reported the growth of submillimetre and millimetre graphene through ambient pressure CVD (APCVD).<sup>11,12</sup>

Generally, the graphene fabricated by CVD on Cu is mainly single-layer because of the self-limited growth of graphene on Cu,<sup>7-12</sup> which can be attributed to the high flow rate of

precursor gas in the growth chamber.<sup>13</sup> At high gas flow rate, only the precursor gas molecules adsorbed on the Cu substrate have enough time to convert to activated carbon atoms with the catalysis of Cu to form graphene. While those far away from the Cu substrate could not make it because of the short residence time and the absence of the catalysis of Cu, causing the lack of activated carbon atoms for the graphene growth, so only single-layer graphene could be formed on Cu by CVD.

To break the self-limited growth of graphene on Cu, Yan K. et al. introduced a second growth process to LPCVD with a tritemperature-zone furnace and made graphene grow layer by layer epitaxially.<sup>14</sup> However, the repeated heating and cooling process may deteriorate the intrinsic property of graphene to some extent. Although Robertson A. W. et al. and Bin W. et al. fabricated few-layer graphene domains on Cu in one-step growth, <sup>15,16</sup> they did it by APCVD and the introduction of abundant high-purity H<sub>2</sub> and CH<sub>4</sub> into the CVD chamber to sustain the ambient pressure could also increase the fabrication cost. Since there are still problems in the study of breaking the self-limited growth of graphene on Cu to grow few-layer graphene by LPCVD, further study is still needed.

In this work, a modified LPCVD (M-LPCVD) method was proposed to fabricate large-grain single-crystal few-layer graphene domains on Cu foils at 1045°C with methane (CH<sub>4</sub>) as the carbon containing precursor gas, breaking the self-limited growth of graphene successfully. The nucleation and growth

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processes of few-layer graphene were studied systematically, and a growth model was proposed as well.

### 2 Experimental

### 2.1 Experimental setup

The fabrication of few-layer graphene on Cu foils was carried out in the M-LPCVD setup (Fig. 1b). As shown in Fig. 1b, to the conventional LPCVD setup (Fig. 1a) we introduced an assembly, which consisted of two 110 mm long quartz tubes: quartz tube-2 with an outer diameter of 18 mm was inserted into the quartz tube-1 with an inner diameter of 19 mm and the length of the overlap was ~100 mm. It is in quartz tube-2 that the Cu substrate was placed. The whole assembly was placed into the conventional LPCVD chamber, i.e. a quartz tube of 200 mm in diameter.



**Fig. 1** Schematics of the conventional LPCVD setup (a), the M-LPCVD setup for few-layer graphene growth (b) and mass-transfer process of CH<sub>4</sub> in the assembly of the two quartz tubes (c).  $C_0$  represents the concentration of CH<sub>4</sub> in the main gas flow and  $C_{\infty}$  the concentration of CH<sub>4</sub> on the surface of Cu substrate.

During the growth process of graphene, the assembly of the two quartz tubes could create a quasi-closed condition for graphene growth, so the mass exchange between the outside and the inside of the assembly proceeds mainly through molecular diffusion driven by the concentration difference between the inside and the outside of the assembly, i.e.  $(C_0 - C_{\infty})$ , as shown in Fig. 1c. In general, the mass transfer by molecular diffusion is a very slow process, so the gas flow rates of H<sub>2</sub> and CH<sub>4</sub> in the assembly are very low, making CH<sub>4</sub> molecules in the assembly have enough residence time to convert to activated carbon atoms, which are the source materials for the

formation of few-layer graphene. Meanwhile, the assembly could also prevent the Cu substrate from being exposed directly to the gas flows of H<sub>2</sub> and CH<sub>4</sub>, so some Cu gas molecules might be trapped in the assembly, which could catalyze the decomposition of CH<sub>4</sub> into gaseous activated carbon atoms in gas phase, promoting the nucleation and growth of adlayer graphene on the growing graphene. Moreover, the masstransfer flux of CH<sub>4</sub> from the main gas flow to the Cu substrate surface in the assembly is not only proportional to the difference between the concentration of CH<sub>4</sub> in the main gas flow (C0) and that on the surface of Cu substrate (C<sub>∞</sub>), i.e. (C<sub>0</sub>-C<sub>∞</sub>) (Fig. 1c), but also proportional to the cross-sectional area of the gap between the two quartz tubes, increasing the controllability of the graphene growth.

### 2.2 Materials preparation

The substrate, 25  $\mu$ m-thick Cu foils (99.8% purity, Alfa Aesar Company) were electrochemically polished in a mixture of 100 ml di-ionized water, 50 ml orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>, purity: 85.0%), 50 ml ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH, purity: 99.6%), 10 ml isopropyl alcohol (C<sub>3</sub>H<sub>8</sub>O, purity: 99.8%) and 1 g urea ((NH<sub>2</sub>)<sub>2</sub>CO, purity: 99.8%) at a voltage of 3.5 V for 2 min. Then the Cu foils were washed by de-ionized water for 1 min and dried by a nitrogen flow for 5 min sequentially. High-purity methane (CH<sub>4</sub>, purity>99.999%) and hydrogen (H<sub>2</sub>, purity>99.999%) were used as the carbon containing precursor and the carrying gas, respectively.

### 2.3 Fabrication process

The few-layer graphene were prepared as follows: firstly, the prepared Cu foils were loaded into the modified setup (Fig. 1b) and then the reaction chamber was evacuated to ~0.01 Pa by opening the vacuum valve completely. After 5 sccm H<sub>2</sub> was introduced into the system, the temperature was increased to  $1045^{\circ}$ C in 45 min. Then the flow rate of H<sub>2</sub> was increased to 100 sccm and at the same time 5 sccm CH<sub>4</sub> was introduced into the chamber for 150 min at 200 Pa. When the growth process ended, the heating power was cut off and the upper lid of the furnace was opened ajar to cool the Cu foils to room temperature rapidly with the flow rates of H<sub>2</sub> and CH<sub>4</sub> unchanged.

### 2.4 Characterizations

The fabricated few-layer graphene was firstly observed by scanning electronic microscopy (SEM, JEM6360-LV, 15 KV). Then the surface of the graphene-on-Cu was coated by spinning with poly-methyl methacrylate (PMMA) and after the Cu substrate was dissolved in a 0.068 g/ml ammonium persulfate solution overnight, a free-standing PMMA-graphene membrane could be obtained, which could be placed on the desired substrates SiO<sub>2</sub>/Si with SiO<sub>2</sub> of 300 nm thickness and TEM grid. Both optical microscopy (OM) and Raman spectroscopy (RS, Jobin Yvon LavRam HR-800, with laser excitation of 514 nm and spot size of 1-2  $\mu$ m) were used to characterize the transferred graphene. High-resolution transmission electron microscopy (HRTEM, JEM-2100, 120 kV acceleration voltage)

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was used to characterize the structure characteristics of the fewlayer graphene.

### 3 Results and discussion

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Fig. 2 shows that most graphene domains are quasi-hexagonal with slightly dendritic edges, which is quite different from that fabricated by the conventional LPCVD, by which the graphene usually takes on six-lobe, four-lobe or quadrangle shapes with much more dendritic edges,<sup>8,17,18</sup> indicating the assembly of the two quartz tubes in Fig.1b does impact the growth of graphene. Moreover, the different contrasts, the "dark" colour and the "grey" colour with respect to the light grey Cu substrate indicate different layers.<sup>15</sup>



Fig. 2 (a) Low-magnification and (b) high-magnification SEM images of the graphene domains grown for 150 min at 200 Pa on Cu foils.

The OM images of few-layer graphene transferred onto  $SiO_2/Si$  substrate exhibit different contrasts more clearly. Fig. 3a shows three contrast colours: light grey, medium grey and dark grey, which represent the  $SiO_2/Si$  substrate, single-layer graphene and bi-layer graphene respectively. In Fig. 3b and 3c appear six contrasts, indicating the existence of one- to five-layer graphene.<sup>19,20</sup>



Fig. 3d-f show Raman spectra from different positions of few-layer graphene domains on SiO<sub>2</sub>/Si substrate. The intense G peaks and 2D peaks indicate the presence of graphene, and the absence of D peaks indicates their good quality.<sup>18,20</sup> Fig. 3d represents Raman spectra from 1- and 2-positions in Fig. 3a. In 1-Raman spectrum, the 2D peak (at ~2680 cm<sup>-1</sup>) with the fullwidth half-maximum (fwhm) ~33 cm<sup>-1</sup> could be well fitted with a single Lorentzian profile and the I<sub>2D</sub>/I<sub>G</sub> ratio was 3.45, identifying the single-layer nature of the graphene.7,16,18 Furthermore, the  $I_{2D}/I_G$  ratio (3.45) is larger than that of singlelayer graphene (~2.5) fabricated by conventional LPCVD method, implying the improved crystallinity.<sup>7,8</sup> In 2-Raman spectrum, the 2D peak is at  $\sim$ 2695 cm<sup>-1</sup> with the fwhm  $\sim$ 51 cm<sup>-1</sup>. which could be well fitted with four Lorentzian profiles, identifying its bi-layer nature with Bernal stacking.<sup>15,21</sup> Moreover, the  $I_{2D}/I_G$  ratio (1.36) also indicates the graphene in 2-position is bi-layer graphene.<sup>21</sup>

Fig. 3e shows Raman spectra in 3-7 positions in Fig. 3b. The 3- and 4-Raman spectra are identical to 1- and 2-Raman spectra, respectively, indicating the graphene in 3- and 4-positions are single-layer and bi-layer graphene respectively. The  $I_{2D}/I_G$  ratios of 5-, 6- and 7-Raman spectra are smaller than 1 and decrease from 0.81 to 0.46, indicating the few-layer nature of graphene in these positions with the fwhms being 67, 69 and 71 cm<sup>-1</sup>, respectively. Moreover, the evolution of the broadening and up-shift 2D peaks coincides with that deduced by Ferrari A. C., implying that they are three-, four- and five-layer graphene with Bernal stacking.<sup>21,22</sup>

Fig. 3f shows Raman spectra in 8- to 12-positions in Fig. 3c. The 8- and 9-Raman spectra are identical to 1- and 2-Raman spectra, indicating the graphene in 8- and 9-position is singleand bi-layer graphene with Bernal stacking, respectively. The position of 2D peak and the  $I_{2D}/I_G$  ratio (2699 cm<sup>-1</sup> and 0.92, respectively) of the 10-Raman spectrum are similar to that (2695 cm<sup>-1</sup> and 0.81, respectively) of the 5-Raman spectra, but the symmetry of the former is worse, indicating that in 10position there may be a large stress, which may do harm to the quality of the graphene. It is interesting that in 11- and 12-Raman spectra, the intensities of 2D peaks increase greatly, resulting in the  $I_{2D}/I_G$  ratios increasing to 2.86 and 2.67 and the fwhms decreasing to 24 and 26 respectively, which suggest that the graphene here is similar to single-layer graphene exfoliated from highly oriented pyrolytic graphite.<sup>23</sup> However, the colour contrasts in Fig. 3c demonstrate they are of few-layer nature.<sup>19,20</sup>

The inconsistency between the Raman spectra and the OM images in 11- and 12-position may be attributed to the turbostratic stacking of few-layer graphene,<sup>24,25</sup> which origins from the accumulating stress of the mismatch of graphene lattice near the nucleation site. Fig. 4b shows HRTEM image of a small area near the nucleation centre (labelled by the dotted box in Fig. 4a), where appear many wrinkles, implying large lattice stress has generated.26 During the growth process of fewlayer graphene, the irregular dimensions of the nucleation sites (hetero particle, dislocations or other type of defects) may push carbon atoms some distance away from their accurate Bernal stacking lattice site, inducing the generation of the lattice stress. As the graphene layers increase, the lattice stress would accumulate gradually. When it increases to a critical value, the carbon atoms in the latter graphene layers would be pushed away from their Bernal stacking lattices sites, forming turbostratic stacking. After the lattice stress was released by forming turbostratic stacking or wrinkles, the crystallinity of the graphene would become better again. As shown in Fig.4c and 4d, there is fewer or even no wrinkles at the sites far away from the nucleation centre, which implies that the quality of graphene is becoming better and better as the distance away from the nucleation centre becomes larger.



Fig. 4 (a) TEM image of a small few-layer graphene nucleus. (b-d) HRTEM images of different areas labeled by b, c and d in (a), respectively.

In general, graphene grown on Cu by LPCVD tend to be single-layer in four- or six-lobed shape because of the self-limited growth mechanism.<sup>7,24</sup> However, in our experiments, we obtained few-layer graphene in approximately hexagonal shape. To study this phenomenon, we conducted a series of experiments for graphene growth under the same condition as that in part 2.2, and the only different parameter is the growth time.



Fig. 5 (a-e) Low-magnification SEM images of the few-layer graphene grown for 5, 10, 20, 40 and 60 min, respectively. (f-g) High-magnification SEM images of the areas labeled by squares in (a) and (b), respectively.

Fig. 5a-e show the SEM images of the few-layer graphene grown for 5, 10, 20, 40 and 60 min, respectively. The dark contrast areas are graphene domains formed on the grey copper

surface. It is found that with the growth time increasing, the graphene domain enlarges while its density decreases, which indicates some imperfect graphene nuclei disappear. After 5

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min growth, as shown in Fig. 5f, there are large amounts of white granules adjoining the growing graphene. When the graphene grows for 10 min, as shown in Fig. 5g, the white granules disappear, leaving some small irregular graphene nuclei randomly distributing around the large graphene domains. As the growth time increases, the area around the growing graphene domains becomes clean (Fig. 5c-e).

The change of the density of the graphene domains and the disappearance of the white granules imply the concentration of carbon species decreases with the growth time increasing until a dynamic equilibrium between the mass transfer of carbon species to the surface of Cu substrate and the carbon species consumed by graphene growth is obtained. The decrease of the concentration of carbon species in the assembly can depress further nucleation, and the dynamic equilibrium can guarantee the graphene nuclei to grow in polygonal shape.



Fig. 6 OM images of few-layer graphene transferred on  $SiO_2/Si$  after growing for 5 min (a) and 10 min (b), respectively.

Fig. 6 shows OM images of the few-layer graphene transferred onto  $SiO_2/Si$ . Because of the relatively high concentration of carbon species in the growth chamber at the

initial growth stage, few-layer graphene starts to nucleate (Fig. 6a). With the decrease of the concentration of carbon species, the nuclei tend to grow into polygonal domains (Fig. 6b).

Theoretically, the activated carbon atoms, which are converted from carbon species, provide necessary carbon sources for the growth graphene. In the conventional LPCVD growth process, the carbon species in the growth chamber are of high flow velocity, so only the carbon species molecules adsorbed on the Cu substrate could be pyrolysized into activated carbon atoms with the catalysis of Cu.7,14 While the carbon species molecules far away from the Cu substrate could not convert to activated carbon atoms because of the short residence time and the absence of the catalysis of Cu, which makes the formation of few-layer graphene impossible. Therefore, only single-layer graphene adjoining the Cu substrate could be formed in the conventional LPCVD. However, in the M-LPCVD system, the assembly of the two quartz tubes can help create a quasi-closed condition, where the flow velocity of the carbon species decreases greatly and some Cu gas molecules might be trapped in the growth chamber, so not only can the carbon species adsorbed on Cu substrate convert to activated carbon species, but those far away from the Cu substrate can also have enough time to convert to gaseous activated carbon atoms with the catalysis of Cu vapor molecules. And these gaseous activated carbon atoms could be adsorbed onto the Cu substrate or the surface of the grown graphene, promoting the nucleation and the growth of adlayer graphene on the grown graphene.



Fig. 7 OM images of few-layer graphene on SiO2/Si substrate after growing for 5 min (a) and 10 min (b), respectively. (c) SEM image of a representative few-layer graphene on Cu foils after growing 20 min. (d-e) Schematic of the growth mechanism of few-layer graphene: d) Nucleation and growth of few-layer graphene at the initial stage; e) Growth of few-layer graphene at the growth stage.

Based on the above analysis, a growth model of few-layer graphene in the M-LPCVD is proposed. As illustrated in Fig. 7, at the initial growth stage, because the concentration of carbon species is high, abundant activated carbon atoms on the Cu substrate and in the gas phase are generated with the catalysis of Cu or Cu vapor molecules, resulting in the nucleation and growth of few-layer graphene by concentration fluctuation or heterogeneous nucleation mechanism (Fig. 7d).<sup>10</sup> As the

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nucleation and the growth process continues, carbon species are consumed continuously, leading to its concentration ( $C_{\infty}$ ) on the surface of Cu substrate gradually decreases to a critical value, less than which no more nuclei can form on the growing graphene layer. However,  $C_{\infty}$  could not always decrease because there is a concentration difference ( $C_0$ - $C_{\infty}$ ) of carbon species between the inside and the outside of the assembly, driving some carbon species diffusion into the assembly. With  $C_{\infty}$  deceasing, the consumption rate of carbon species decreases while  $C_0$ - $C_{\infty}$  increases gradually, leading to the mass-transfer flux of carbon species into the assembly increase. When the consumption rate of carbon species becomes equal to the masstransfer flux of carbon species into the assembly, a dynamic equilibrium is obtained, which can guarantee few-layer graphene nuclei to grow steadily (Fig. 7e).

### Conclusions

Few-layer graphene were fabricated on Cu foils by introducing an assembly to the conventional LPCVD method, successfully breaking the self-limited growth of graphene by LPCVD. SEM, OM, Raman spectroscopy and HRTEM were used to characterize the fabricated graphene domains. The results indicated that the graphene were one- to five-layer graphene with good quality, and the few-layer graphene could take on Bernal stacking or turbostratic stacking order determined by the magnitude of the stress at the nucleation centre. On the basis of the growth characteristics of graphene, a growth mechanism was proposed. We believe this method could provide theoretical and engineering researchers with good-quality fewlayer graphene, accelerating study on fundamentals and applications of single-crystal few-layer graphene.

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### Notes and references

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Few-layer graphene domains are fabricated by modified LPCVD on Cu and the growth mechanism was schematically shown in the figure.