RAPID COMMUNICATION

Influence of reaction parameters on synthesis of high-quality single-layer graphene on Cu using chemical vapor deposition*

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Large-area monolayer graphene samples grown on polycrystalline copper foil by thermal chemical vapor deposition with differing CH_4 flux and growth time are investigated by Raman spectra, scanning electron microscopy, atomic force microscopy, and scanning tunneling microscopy. The defects, number of layers, and quality of graphene are shown to be controllable through tuning the reaction conditions: ideally to 2–3 sccm CH_4 for 30 minutes.

Keywords: graphene, chemical vapor deposition, Raman spectra

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1. Introduction

Graphene, a two-dimensional (2D) sheet of sp^2-hybridized carbon atoms, has been the focus of much research because of its distinctive band structure and other physical properties, which make it useful in many possible applications, such as, optoelectronics, energy storage, especially in electronics.[1–9] Therefore, the fabrication of large-area high-quality graphene is important for its potential application. In the past decades, various routes have been used to prepare graphene.[10–18] Among these methods, chemical vapor deposition (CVD) maybe is the most promising approach for its simplicity, low cost, and relatively large yield. In the CVD process, the growth parameters are crucial: catalyst, carbon source, pre-treatment of substrate, reaction temperature, pressure, gas flow rates, etc. Therefore, the CVD growth parameters determine graphene's quality, uniformity, and number of layers. Kong *et al.*[19] reported that the reaction pressure affects both large area thickness uniformity and defect density. Chen's group found that the quality and number of layers of graphene can be controlled by H_2 concentration.[20] Furthermore, different shapes of graphene were obtained by Liu's group through varying the reaction conditions.[21] However, in previous reports, larger flow rates of methane and hydrogen gas were used in growth process. The influence of lower flow rates of methane on graphene growth is generally unknown. In the present work, we synthesized high-quality and large-area monolayer graphene under lower flow rates of methane (2–3 sccm). We investigated the influence of flow rates of methane and reaction time on the growth of monolayer graphene under approximate ambient pressure. The morphology, defects, and structure of graphene were characterized by using scanning electron microscopy (SEM), Raman spectra, atomic force microscopy (AFM), and scanning tunneling microscopy (STM). The results indicate, unsurprisingly, that the quality and morphology of graphene depend on the growth factors. The details of these dependencies are discussed after describing the experiment.

2. Experimental section

2.1. Materials

Polycrystalline copper foils (0.25 mm thick, 99.98 wt.%) were purchased from Sigma-Aldrich Company. Methane (CH_4, 99.99 vol.%), argon (Ar, 99.99 vol.%), and H_2/Ar (H_2, 10 vol.%) were purchased from Beijing Praxair Application Gas Co., Ltd. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, AR) was purchased from Sinopharm Chemical Reagent Co.

2.2. Synthesis of graphene

Graphene was grown in KLG-12Y quartz tube furnace. First, a copper foil as catalytic substrate was loaded into a quartz tube furnace and heated up to 1050 °C under 200 sccm Ar and 100 sccm H_2/Ar (H_2, 10 vol.%). After the reaction temperature reached 1050 °C, the Cu foil was annealed for 30 min under the same gas flow rates. Then graphene was grown at 1050 °C under a gas mixture of CH_4 and 100 sccm of H_2/Ar at 10^4–10^5 Pa. Finally, the sample was cooled down to room temperature in the furnace under 200 sccm Ar and 100 sccm H_2/Ar.

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2.3. Transfer procedure

The transfer of graphene was carried out as in previous work.[22] A drop of poly(methyl methacrylate) (PMMA) solution was spin-coated onto the surface of the graphene, still on copper foil. The first rev is at about 600 r.p.m. for 10–15 seconds and the second rev is at about 3000 r.p.m. for 1 minute. Then the PMMA covered graphene was heated at 180 °C for 1 minute. The sample was put into 0.05 g/mL iron chloride ($FeCl_3$) aqueous for etching. After about 20 hours, the copper substrate was dissolved completely. The PMMA/graphene stack was cleaned three times with deionized water. The sample was laid on the target substrate and dried at 80 °C for 20 minutes. A new drop of PMMA 950 solution was spin-coated onto the PMMA/graphene to redissolve and relax the pre-coated PMMA. At room temperature, the PMMA/graphene film was then slowly cured for about half an hour, and the PMMA was finally dissolved by acetone.

2.4. Characterization

The morphology of the graphene was obtained by using a scanning electron microscope (SEM, Raith 150 with a working voltage of 10 kV) and atomic force microscope (AFM, Veeco Nanoscope IIIa with a Si tip), respectively. The atomic resolution image of graphene was obtained with a scanning tunneling microscope (STM, Veeco Nanoscope IIIa with a Pt–Ir alloy tip). Raman spectrometer (Horiba Jobin Yvon LabRAM HR 800 with a laser wavelength of 532 nm, power of 1 Mw, beam spot diameter of 1 μm, and a 100× objective lens) was used to detect the number of layers of the graphene.

3. Results and discussion

3.1. Effect of methane flux and reactive time on growth of graphene

3.1.1. Effect of methane flux on growth of graphene

The CVD growth of graphene on Cu foil can be described in terms of surface adsorption, which is due to the low carbon-solubility of Cu.[23] In order to understand the influence of gas flux on the nucleation of graphene on Cu foil, different flow rates of methane (CH_4) were used to prepare graphene. Figure 1 shows the SEM images of graphene grown under different flow rates of CH_4 (0.5–3 sccm CH_4, see Figs. 1(a)–1(f), respectively). In all the reactions, H_2/Ar mixed gas flow (H_2, 10 vol.%), temperature and pressure of growth are kept at 100 sccm, 1050 °C, and 10^4–10^5 Pa, respectively. From Fig. 1(a), it is seen that only a few carbon nuclei are formed on the Cu foil at a CH_4 flow rate of 0.5 sccm. The density and size of graphene nucleation gradually increase with increasing CH_4 flux. The crystal nuclei of graphene become larger, and domains of graphene grains tend to form hexagons under 1.5 sccm CH_4 (Fig. 1(c)). The grains of graphene rapidly form a continuous and uniform single layer when CH_4 flux is larger than 1.5 sccm. These results indicate that only tenuous nucleation of graphene occurs at lower CH_4 flow, due to the scarcity of source carbon, which results in the formation of small clusters on the surface of the Cu foil. With increasing flow of CH_4, hexagons of graphene are obtained. Finally, continuous and uniform monolayer graphene film forms under sufficient CH_4 flux. Compared to other groups' approaches, we find that using lower CH_4 flux produces highly uniform, continuous graphene.

In order to evaluate graphene samples prepared under different CH_4 flow rates for their quality, defects and number of layers, we use Raman spectra. From Fig. 2(a), it is seen clearly that weak G and 2D peaks appear at lower flow rates, which indicates the formation of small graphene grains. The intensity of G and 2D peaks becomes stronger gradually with increasing CH_4 flux. The positions of G and 2D peaks are located at about 1590 cm^{-1} and 2700 cm^{-1}, receptively, and do not shift with the CH_4 flow rate. The weaker D peaks are observed for all flow rates. These results demonstrate that different sizes (i.e., dots, hexagons, and continuous sheet) of graphene can be formed under different CH_4 flux.

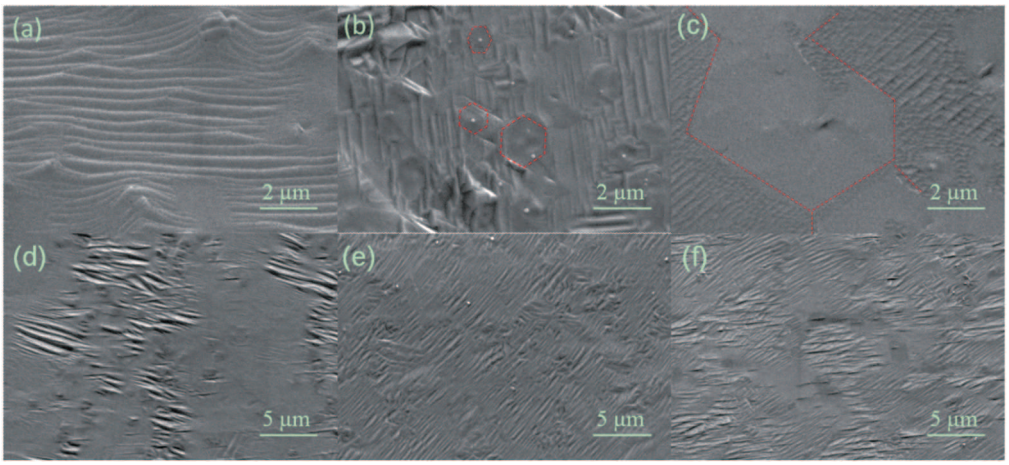

Fig. 1. (color online) Typical SEM images of graphene on Cu foil at 1050 °C for 30 minutes under a gas mixture of 100 sccm of H_2/Ar and different fluxes of CH_4: (a) 0.5 sccm; (b) 1 sccm; (c) 1.5 sccm; (d) 2 sccm; (e) 2.5 sccm; (f) 3 sccm.

The graphene samples were transferred from the Cu foil onto 300-nm SiO_2/Si substrate using a chemical etching method. The Raman spectra of graphene are shown in Fig. 2(b). From the curve (i), we observe not only G and 2D peaks, but also a D peak, revealing that a lot of defects exist in graphene grown under 0.5 sccm CH_4. On the other hand, the intensity of D, G, and 2D peaks is weaker, which proves that smaller grains of graphene form in this condition, consistent with the SEM result (Fig. 1(a)). The intensity rate of 2D to G, I_{2D}/I_G, gradually increases with increasing CH_4 flow rate, varying from about 3 to 4 when the flow rate is changed from 1.0 sccm to 3.0 sccm. These results indicate that uniform and continuous single-layer graphene with fewer defects forms under low (2–3 sccm) CH_4 flux.

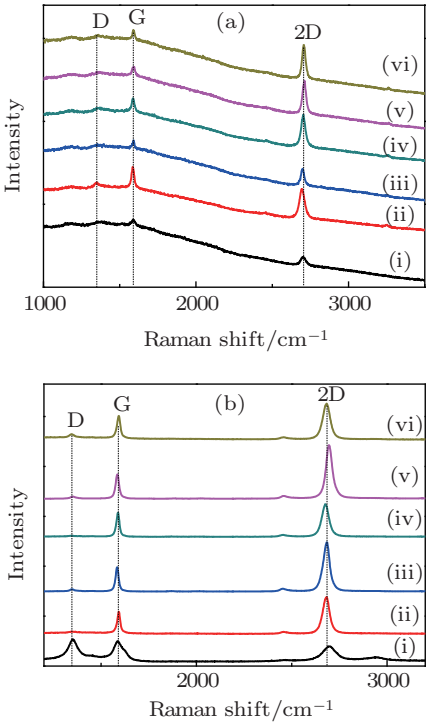

Fig. 2. (color online) (a) Raman spectra of graphene grown on Cu foil at 1050 °C for 30 minutes under a gas mixture of 100 sccm of H_2/Ar and different fluxes of CH_4; (b) Raman spectra of graphene after it is transferred onto SiO_2/Si substrate. (i) 0.5 sccm; (ii) 1 sccm; (iii) 1.5 sccm; (iv) 2 sccm; (v) 2.5 sccm; (vi) 3 sccm.

3.1.2. Effect of reaction time on growth of grapheme

We also investigate the effect of different reaction time on growth of graphene. Figure 3(a) shows the Raman spectra of graphene growth on Cu foil in 100 sccm of H_2/Ar (H_2, 10 vol.%) at the reaction temperature of 1050 °C for different growth times: 5 min, 15 min, 25 min, 30 min, and 35 min. The flow rate of CH_4 is constant: 3 sccm. It is seen that the signals of G and 2D peaks appear for all growth times. Due to strong background scattering of Cu foil in Raman spectra, the Raman peaks in Fig. 3(a) are weaker. Therefore, we transfer graphene from Cu foil onto 300-nm SiO_2/Si substrate and Raman analysis is shown in Fig. 3(b). Compared with Raman spectra of graphene grown on Cu foil, we find that the intensity of G and 2D peaks increases substantially and the 2D peak position shows a red-shift. These phenomena may derive from the different thermal expansion between the as-grown graphene and graphene supported by a different substrate material.[24] Intensity ratio I_{2D}/I_G is about 3, and has symmetric 2D band with a full width at half maximum of ~35 cm^{-1}, indicating the formation of monolayer graphene in each sample. However, there are a lot of defects in sample prepared during a short reaction time. On the other hand, prolonged reaction times result in the formation of bilayer or few-layer graphene. Figure 4 shows the SEM images of graphene prepared at 5 min, 15 min, and 30 min, respectively. It can be seen that small graphene grains form during a reaction of 5 min (marked with dashed line in Fig. 4(a)). An almost continuous monolayer graphene is obtained with a growth time of 15 min, but we find that some zones are not covered (marked with dashed red line in Fig. 4(b)). At 30 min, not only continuous single layer graphene but also bilayer or multilayer graphene can be found (marked with dash red line in Fig. 4(c)). This result is consistent with Raman analysis.

In summary, large-area uniform monolayer graphene films can be obtained on copper foil at 1050 °C for 30 minutes under a gas mixture of 2–3 sccm CH_4 and 100 sccm of H_2/Ar at 10^4–10^5 Pa.

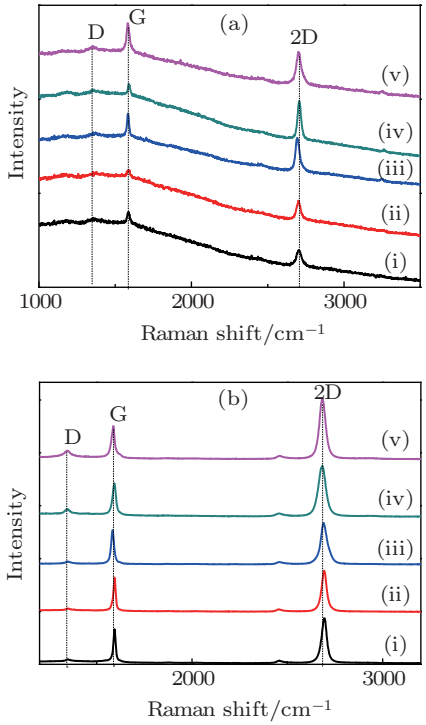

Fig. 3. (color online) (a) Raman spectra of graphene grown on Cu foil at 1050 °C under a gas mixture of 3 sccm CH_4 and 100 sccm of H_2/Ar for different growth times. (b) Raman spectra of graphene after it is transferred onto SiO_2/Si substrate. (i) 5 min; (ii) 15 min; (iii) 25 min; (iv) 30 min; (v) 35 min.

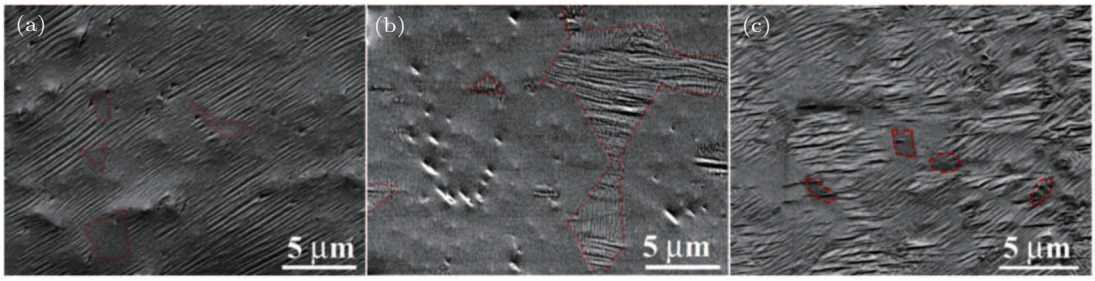

Fig. 4. (color online) SEM images of graphene grown on Cu foil at 1050 °C under a gas mixture of 3 sccm CH_4 and 100 sccm of H_2/Ar for different growth times: (a) 5 min; (b) 15 min; (c) 30 min.

3.2. Quality and atomic structure of monolayer graphene

In order to evaluate the quality of graphene prepared under the above mentioned optimal growth parameters, we observed surface morphology, atomic structure, and defects of graphene using AFM, STM, and Raman mapping at room temperature.

Figure 5 shows the AFM and atomic resolution STM images of graphene on Cu foil. From the AFM image (Fig. 5(a)), it is found that, although there are some terraces on the surface of Cu foil, the growth of graphene is still continuous across the corrugated stepped surface and grain boundaries of Cu foil. Furthermore, the atomic resolution STM image (Fig. 5(b)) of graphene on Cu foil presents a typical honeycomb structure, in which the six carbon atoms of the six-member rings appear with equal intensity and are equivalent, a typical feature of monolayer graphene. The inset diagram (Fig. 5(b)) shows a line profile taken along the blue line, illustrating the periodic structure of graphene, with a lattice constant of about 0.25 nm. Although some fluctuation is observed, the lattice is defect-free. This result indicates that graphene prepared by the CVD can have high crystal quality.

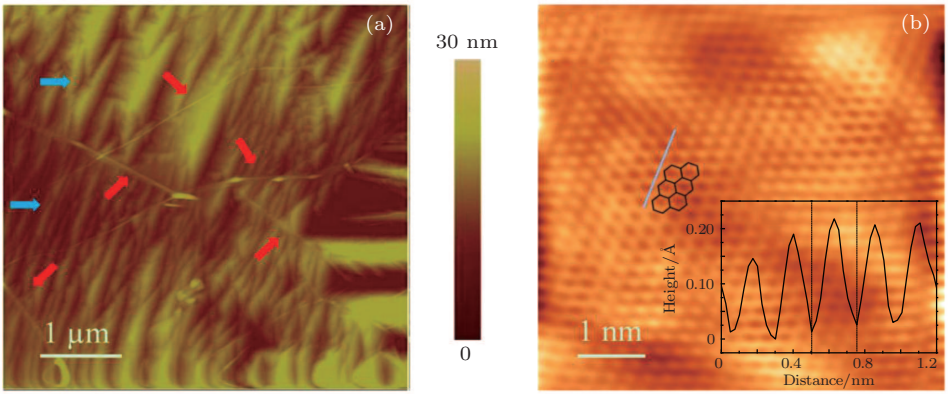

Fig. 5. (color online) (a) AFM height image (Cu steps: blue arrows; wrinkles of graphene: red arrows) and (b) atomic resolution STM image (tunneling current $I_t = 1.5$ nA, sample-tip bias voltage $V_{bias} = -1.0$ V) of graphene on Cu foil. Inset in panel (b) shows the line profile taken along the blue line. Growth conditions: 1050 °C for 30 minutes under a gas mixture of 2.5 sccm CH_4 and 100 sccm of H_2/Ar.

Figure 6 shows a Raman spectrum of graphene after it is transferred onto 300-nm SiO_2/Si substrate. Stronger G and 2D peaks located at ∼1591 and ∼2683 cm^{-1}, respectively, are observed. A weaker D peak at 1345 cm^{-1} is also found. The intensity ratio of I_{2D}/I_G is about 3.5. These results indicate that monolayer graphene is obtained. As shown in the inset of Fig. 6, the 2D peak can be fitted with a single sharp Lorentz peak and the full width at half maximum of a 2D band is ∼30 cm^{-1}, which are typical features of a single-layer graphene.

Further Raman mapping analysis of graphene is shown in Fig. 7. The length of one step is 0.5 microns and the area of the whole scan is 4.5 μm×5.5 μm. Raman mapping of the

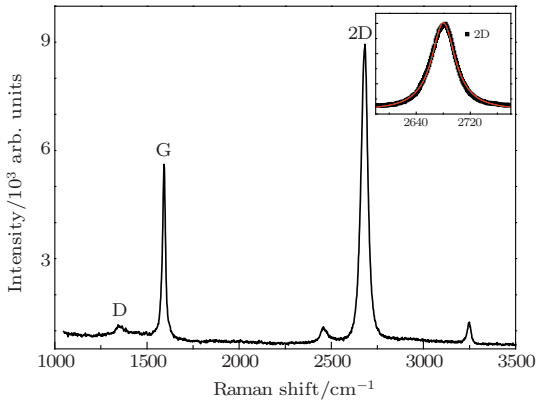

Fig. 6. (color online) Raman spectrum of graphene transferred onto SiO_2/Si wafer. The inset shows a single sharp Lorentz peak after fitting the 2D band with Lorentz peaks. Growth conditions: 1050 °C for 30 minutes under a gas mixture of 2.5 sccm CH_4 and 100 sccm of H_2/Ar at 10^4–10^5 Pa.

G band (centered at about 1584–1589 cm^{-1}, see Fig. 7(a)) with a full width at half maximum of about 18 cm^{-1} suggests that there is little intrinsic doping in the graphene films.[25] Symmetric 2D bands (centered at about 2689–2710 cm^{-1}, see Fig. 7(b)) have full widths at half maximum of about 33 cm^{-1}. Raman maps of the intensity ratio of D to G bands (Fig. 7(c)) are very small (about 0.07–0.38), indicating that the defects in graphene are very few. Raman maps of the intensity ratio of 2D/G (Fig. 7(d)) are about 3–4, which is consistent with Raman spectra analysis. Raman mapping results demonstrate that high-quality, continuous single-layer graphene is obtained under the optimized growth conditions.

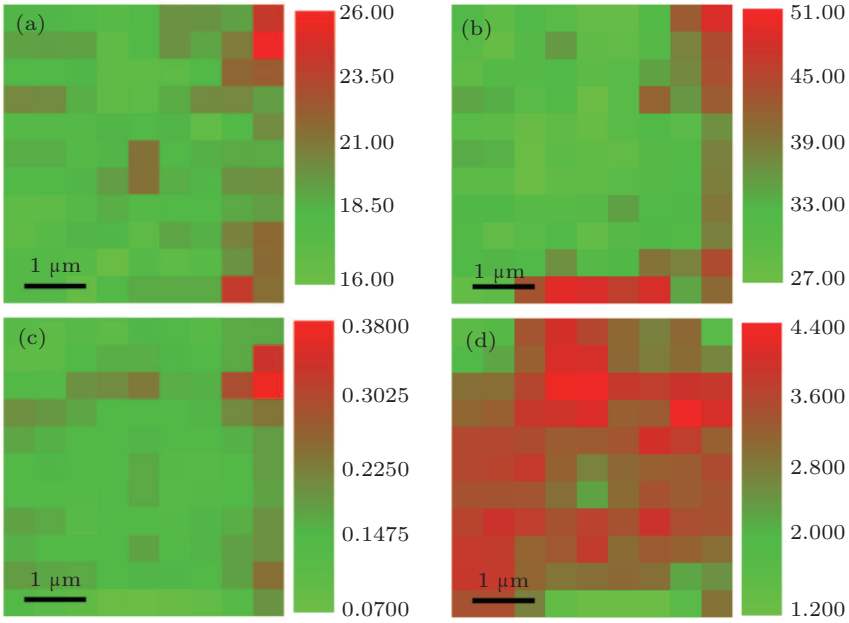

Fig. 7. (color online) Raman maps of (a) full width at half maximum of G bands (1584–1589 cm^{-1}); (b) full width at half maximum of 2D bands (2689–2710 cm^{-1}); (c) the intensity ratio of D/G; (d) the intensity ratio of 2D/G.

4. Conclusion

In summary, large-area monolayer graphene has been grown by chemical vapor deposition (CVD) on polycrystalline copper foil. Optimized growth parameters for high-quality monolayer graphene were obtained through tuning different reaction conditions: 1050 °C for 30 minutes with a gas mixture of 2–3 sccm CH_4 and 100 sccm of H_2/Ar under 10^4–10^5 Pa. The nucleation, quality, morphology, and structure were analyzed using Raman spectra and maps, SEM, AFM, and STM. The results indicate that the layer count and the quality of graphene can be controlled through tuning the reaction conditions.

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