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Control of thickness uniformity and grain size in graphene films for transparent conductive electrodes

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Abstract

Large-scale and transferable graphene films grown on metal substrates by chemical vapor deposition (CVD) still hold great promise for future nanotechnology. To realize the promise, one of the key issues is to further improve the quality of graphene, e.g., uniform thickness, large grain size, and low defects. Here we grow graphene films on Cu foils by CVD at ambient pressure, and study the graphene nucleation and growth processes under different concentrations of carbon precursor. On the basis of the results, we develop a two-step ambient pressure CVD process to synthesize continuous single-layer graphene films with large grain size (up to hundreds of square micrometers). Scanning electron microscopy and Raman spectroscopy characterizations confirm the film thickness and uniformity. The transferred graphene films on cover glass slips show high electrical conductivity and high optical transmittance that make them suitable as transparent conductive electrodes. The growth mechanism of CVD graphene on Cu is also discussed, and a growth model has been proposed. Our results provide important guidance toward the synthesis of high quality uniform graphene films, and could offer a great driving force for graphene based applications.

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene, a two-dimensional crystal that is the building block of all graphitic forms, has been attracting much attention due to its extraordinary properties, such as anomalous quantum Hall effect [1–3], extremely high mobility [4, 5], high elasticity [6], and optical transparency [7]. Such unique properties make graphene a great potential candidate for various applications, e.g., transistors [8–10], transparent electrodes [11–14], and chemical/bio sensors [15–17]. For these purposes, it is critical to synthesize large scale, high quality graphene films. Recent results have shown that chemical vapor deposition (CVD) of hydrocarbons onto relatively inexpensive polycrystalline Ni and Cu substrates is a highly promising approach for producing high quality

graphene on a large scale [18–20]. Moreover, the transfer of graphene grown on Ni and Cu onto arbitrary substrates can be readily achieved since the wet etching of Ni and Cu is feasible and straightforward. Single-layer graphene films up to 30 nm thick grown on Cu have been obtained by Bae *et al* using low pressure CVD [11], and the transferred films show mobilities up to $7350 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at low temperature, and a sheet resistance of $\sim 30 \text{ } \Omega/\text{sq}$ with $\sim 90\%$ optical transmittance for a doped four-layer graphene film (layer-by-layer transfer).

The CVD growth of graphene on Cu substrates has been considered to be surface mediated and somewhat self-limiting due to the extremely low carbon solubility in Cu, leading to the growth of predominantly single-layer films [18, 21]. Recently, however, it has been reported that such self-limiting

growth can be broken under certain CVD conditions (e.g., high growth pressure, large amount of carbon precursor), where massive non-uniform multi-layer graphene films are grown [22, 23]. For a better controlling of thickness and uniformity of CVD graphene films grown on Cu, a detailed understanding of the formation of the multi-layer feature is strongly required. In addition, large scale CVD graphene films produced so far are found to be polycrystalline, consisting of numerous grain boundaries [24, 25]. Our previous work and that of other groups have clearly demonstrated that the grain boundaries in graphene can degrade its electrical and mechanical properties [26–29]. To further envision graphene technology, it will clearly be necessary to synthesize uniform graphene films with large grain size (few or even no grain boundaries). Here, we grow graphene films on Cu foils at 1050 °C by ambient pressure CVD (the high growth temperature is chosen for achieving a low graphene nucleation density), and study the graphene nucleation and growth processes at different concentrations of carbon precursor (CH_4 in this case). On the basis of the results, we develop a two-step ambient pressure CVD technique to synthesize continuous single-layer graphene films with large grain size (up to hundreds of square micrometers). The film thickness and uniformity are confirmed by scanning electron microscopy (SEM) and Raman spectroscopy. We also transfer graphene films (up to four layers, layer-by-layer transfer) on cover glass slips for the measurements of optical transmittance and sheet resistance. The growth mechanism of CVD graphene on Cu is also discussed, and a detailed model is then proposed.

2. Experimental methods

2.1. Graphene growth

Graphene was synthesized by CVD of CH_4 on Cu foils (25 μm thick, 99.8%, Alfa) in a quartz tube furnace at ambient pressure. Before CVD, Cu foils were cleaned by acetone, methanol, and DI water. During CVD, Cu foils were first reduced and annealed in mixtures of Ar and H_2 gases at 1050 °C for 30 min to clean the Cu surface and increase the Cu grain size. Graphene growth was then carried out at 1050 °C by introducing CH_4 of different concentrations (5, 10, 20, 30, 55, 500 ppm) balanced in Ar and H_2 with a total flow rate of 1500 sccm (1.3% H_2). The growth time was varied from 5 to 60 min. After growth, samples were fast-cooled down to room temperature in the protection of Ar and H_2 .

2.2. Graphene transfer

Graphene samples were transferred onto other substrates (glass slips, SiO_2/Si wafers) by a poly(methyl methacrylate) (PMMA)-assisted wet-transfer method [30, 31]. The Cu etchant used was an aqueous solution of iron nitrate (0.1 g ml^{-1}). A thin layer of PMMA (MicroChem 950 PMMA C, 3% in chlorobenzene) was spin-coated on one side of a graphene sample at 3000 rpm for 1 min, which was then cured at 150 °C for 2 min. Graphene grown on the other side of the Cu foil without PMMA cover was removed by O_2 plasma etching. Subsequently, the sample was placed

in 0.1 g ml^{-1} iron nitrate solution to etch off the Cu foil. Typically, the etching process runs overnight. After the Cu foil was completely etched away, graphene with PMMA coating was scooped out from the solution by the target substrate. The PMMA was then removed by acetone and the sample was rinsed several times with DI water. The transfer process was repeated to produce stacks of graphene layers (up to four layers). Although much attention has been paid to each step during the transfer process for clean graphene samples, metal contaminants including Fe, Ca, and Cu can still exist.

2.3. Characterization

SEM (LEO 1525), optical microscopy, and Raman spectroscopy (Triax 550) were used to characterize the graphene samples. The wavelength of the excitation laser was 532 nm and the laser spot size was $\sim 2 \mu\text{m}$ with a $\times 50$ objective lens. The transmittance of the graphene was measured using a spectrophotometer (Hitachi U-2001), where a bare cover glass slip was used as a reference. The electrical conductivity of the graphene samples was measured by the van der Pauw method. The measurements were performed on 1 cm \times 1 cm graphene films transferred onto glass slips with silver paint at four corners of the films as electrodes. Graphene nucleation density and the evolution of film coverage on the Cu surface at different CH_4 concentrations were determined by averaging results from ~ 10 SEM images of different areas on each sample. Graphene grain area was determined from the nucleation density and the final film coverage at each CH_4 concentration.

3. Results and discussion

At the growth stage, the introduced amount of CH_4 greatly influences the graphene nucleation density and the final film coverage on the Cu surface. Figure 1(a) shows graphene coverage on Cu as a function of time at different CH_4 concentrations. At high CH_4 concentrations, Cu surfaces are fully covered by graphene in 20 min for 30 ppm CH_4 and 30 min for 20 ppm CH_4 , respectively. Large numbers of multi-layer graphene domains (mostly bilayer) are observed on both of these samples (figures 2(c) and (d); multi-layer domains are darker). Graphene grown at 20 ppm CH_4 shows multi-layer domains with an average size (linear length) of $\sim 4 \mu\text{m}$, while graphene grown at 30 ppm CH_4 has a higher density of multi-layer domains with an average size of $\sim 2 \mu\text{m}$. At low CH_4 concentration (5 ppm), the Cu surface reaches only $\sim 70\%$ coverage after 60 min (figure 2(a)), and under this condition it will not reach a full coverage even when continuously exposed to CH_4 . Hexagonal-shaped graphene grains are merging together and all show a single-layer feature (uniform film surface contrast in figure 2(a)). In the case of 10 ppm CH_4 , graphene almost fully covers the Cu surface, reaching $\sim 99\%$ after 60 min growth (figure 2(b); the uncovered Cu surface is brighter). Multi-layer graphene domains are seldom observed on this sample.

Figure 1(b) shows graphene nucleation densities and grain areas obtained at 5, 10, 20, and 30 ppm CH_4 . It can be seen that nucleation density increases from 3.48×10^5

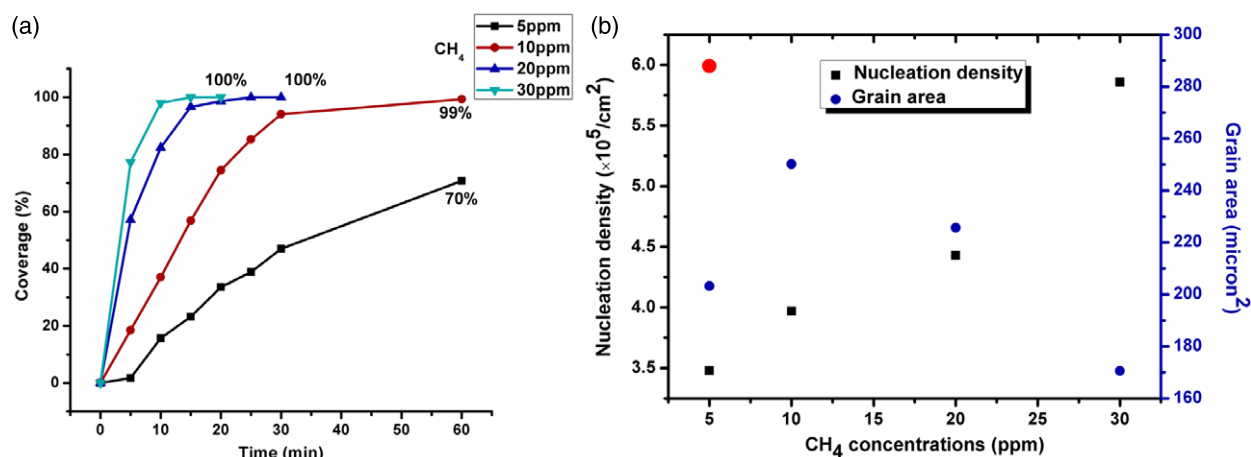


Figure 1. (a) Graphene coverage on Cu as a function of growth time at different CH₄ concentrations (5, 10, 20, 30 ppm). The final coverage under each CH₄ concentration is labeled in the image. (b) Graphene nucleation density and grain size as a function of CH₄ concentration. The red solid circle indicates the expected grain size obtained at 5 ppm CH₄ assuming a full graphene coverage.

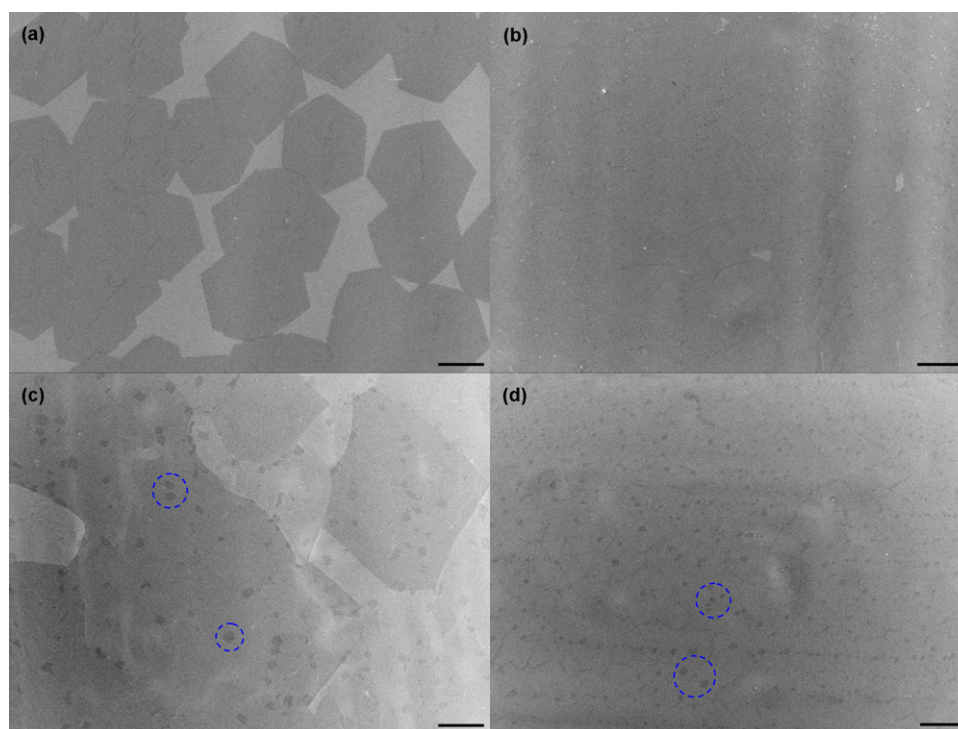


Figure 2. SEM images of CVD graphene on Cu. (a) 5 ppm CH₄ for 60 min. (b) 10 ppm CH₄ for 60 min. (c) 20 ppm CH₄ for 30 min. (d) 30 ppm CH₄ for 20 min. Uncovered Cu surface is brighter (images (a) and (b)). Multi-layer graphene domains are darker (some are highlighted by dashed blue circles in images (c) and (d)). The scale bars are 10 μm .

to $5.86 \times 10^5 \text{ cm}^{-2}$, as the CH₄ concentration increases from 5 to 30 ppm. The higher the graphene nucleation density, the smaller the graphene grains grown. The average grain areas are ~ 170 , ~ 225 , and $\sim 250 \mu\text{m}^2$ obtained at 30, 20, and 10 ppm CH₄, respectively. There is a roughly linear relationship between grain area and the inverse CH₄ concentration. If we assume a full coverage for graphene grown at 5 ppm CH₄, the average grain area could be as large as $\sim 287 \mu\text{m}^2$ (red solid circle in figure 1(b)), which is about twice the reported value of $\sim 142 \mu\text{m}^2$ for grains obtained by low pressure CVD [24].

At high temperatures, a lower density of graphene nucleation enables the growth of large grains [32]. In our experiment, at the given growth temperature of 1050 °C, very close to the melting point of Cu (1083 °C), it is possible that by finding a more appropriate CH₄ concentration, for example between 10 and 20 ppm, graphene films of full coverage and without multi-layer domains could be produced. But in this case, graphene nucleation density would be higher than those obtained at 5 or 10 ppm CH₄, according to the trend shown in figure 1(b).

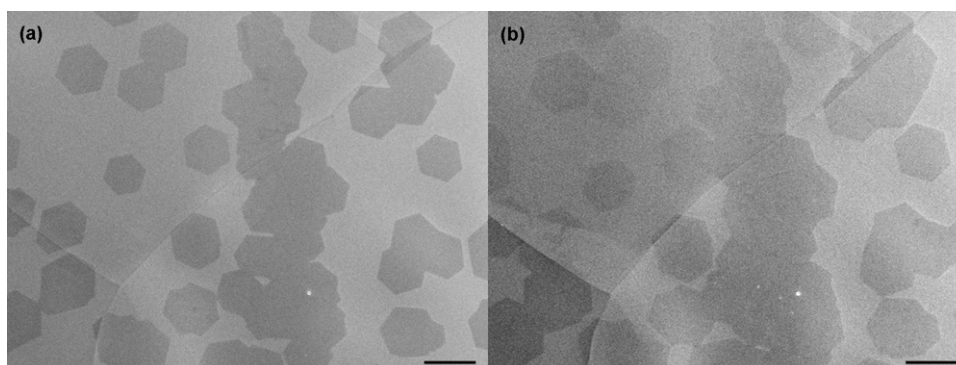


Figure 3. SEM images of as-grown graphene grains on Cu (a) before and (b) after increasing CH_4 concentration. The growth was halted before the formation of a continuous graphene film. Images (a) and (b) were taken in the same area of the Cu. The scale bars are $10\ \mu\text{m}$.

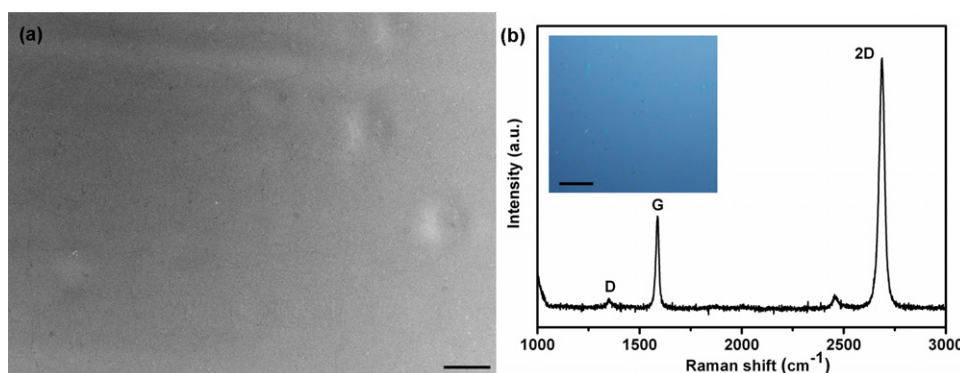


Figure 4. (a) SEM image of as-synthesized graphene film on Cu. The scale bar is $10\ \mu\text{m}$. (b) Raman spectrum of the graphene film on SiO_2/Si substrate. Laser excitation wavelength is $532\ \text{nm}$. Inset: optical image of the transferred graphene on SiO_2/Si . The scale bar is $25\ \mu\text{m}$.

On the basis of the above results and discussion, we developed a two-step ambient pressure CVD process to synthesize continuous graphene films with uniform thickness (single layer) and large grain size (low nucleation density). The two-step CVD parameters are shown in table 1. During deposition, graphene initially nucleates and grows at a low CH_4 concentration (5 ppm), where a low nucleation density is guaranteed. After 20 min, the growth is continued by increasing CH_4 concentration to 55 ppm without changing any other conditions to get a complete graphene coverage. The produced graphene films can have uniform thickness and large grain size. Here, we need to point out that, once the nucleation density is set at low CH_4 concentrations, no significant new graphene nuclei are formed during the second growth step with high CH_4 concentrations. Figure 3(a) shows a SEM image of the graphene grains on Cu grown at the low CH_4 concentration. The grains are grown larger after increasing CH_4 concentration in the second growth step, and no new graphene nucleation is observed (figure 3(b)). The change in growth conditions (CH_4 concentration) may only affect graphene growth rate and final surface coverage.

An SEM image of as-synthesized graphene sample by our two-step CVD technique (figure 4(a), taken directly on the surface of the Cu foil without any processing) shows features of a continuous uniform film with very few multi-layer domains. The film uniformity is also confirmed by an optical

Table 1. Two-step CVD parameters for graphene growth. Prior to deposition, the Cu substrates are annealed at $1050\ ^\circ\text{C}$ for 30 min in a mixture of Ar and H_2 gases. The diluted CH_4 indicates Ar balanced CH_4 of 500 ppm in concentration.

Step	Growth temperature $T\ (^{\circ}\text{C})$	Growth H_2 :diluted CH_4 :Ar in sccm	Growth time t (min)
1	1050	20:15:1465 (5 ppm CH_4)	20
2	1050	20:165:1315 (55 ppm CH_4)	15

image (figure 4(b) inset) of the transferred graphene on a SiO_2/Si substrate, which shows almost no color variation. We further performed Raman spectroscopy measurements on more than 10 randomly chosen locations across the film (transferred onto SiO_2/Si substrate). A representative Raman spectrum (figure 4(b)) shows two primary features, including a G band at $\sim 1587\ \text{cm}^{-1}$ and a 2D band at $\sim 2687\ \text{cm}^{-1}$. The monolayer thickness is verified by a symmetric 2D band with a full width at half-maximum (FWHM) of $\sim 29\ \text{cm}^{-1}$ and a ~ 2.5 2D/G intensity ratio (I_{2D}/I_G) [16, 18, 33]. The D band at $\sim 1351\ \text{cm}^{-1}$ corresponds to defects in the graphene film. The very weak D band in the spectrum with a typical D/G intensity ratio of ~ 0.1 indicates high

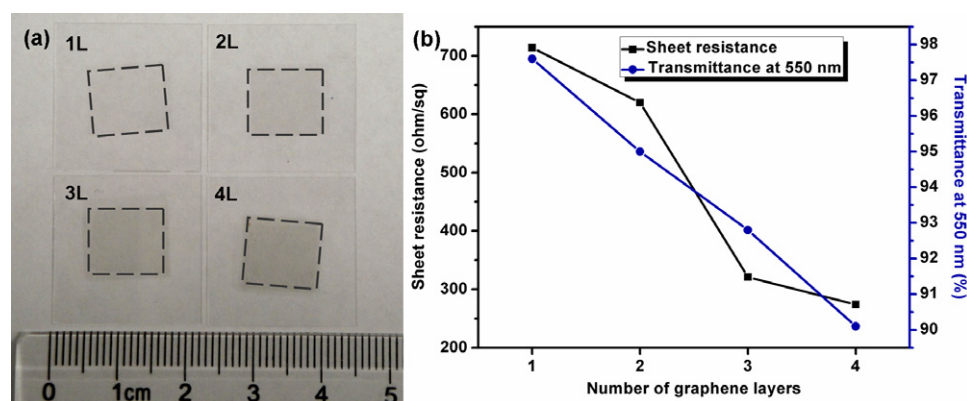


Figure 5. (a) Photograph of 1 cm \times 1 cm layer-by-layer transferred graphene films with one to four layers on cover glass slips. (b) Sheet resistance and optical transmittance at 550 nm of the transferred graphene films as a function of the number of stacked graphene layers.

crystalline quality of the graphene. Such an observable Raman D signal has also been found in the CVD-grown large single crystals of graphene transferred onto SiO₂/Si substrate [34]. We ascribe the emergence of the defect-induced D band in transferred CVD graphene films to the unintentional damage or contamination from the chemical transfer process.

Figure 5 shows the optical and electrical properties of the graphene films synthesized by our two-step ambient pressure CVD. Multiple layers of graphene (up to four layers) are prepared by repeating the PMMA-assisted transfer process, and the obtained stacked graphene films on cover glass slips are shown in figure 5(a). The sheet resistance and optical transmittance at 550 nm as a function of the number of the stacked graphene layers are shown in figure 5(b). One layer of the graphene film absorbs $\sim 97.6\%$, and the transmittance is usually reduced by $\sim 2.4\%$ for an additional transfer, indicating an average thickness of a single layer [7]. The sheet resistance of a single-layer graphene film is $\sim 710 \Omega/\text{sq}$, while that of four layers of the film is $\sim 270 \Omega/\text{sq}$ with $\sim 90.1\%$ transmittance. The results compare well with measured values of $350 \Omega/\text{sq}$ for four-layer CVD graphene with 90% transmittance [12], and $300 \Omega/\text{sq}$ for three-layer CVD graphene with 91.2% transmittance [13]. It should be noted that additional efforts are still needed for best applications as transparent electrodes, including improving the transfer process, and chemically doping graphene [11].

The CVD growth of graphene on Cu occurs by a surface adsorption process due to the extremely low solubility of carbon in Cu. The growth is considered to be self-limiting, where the produced films are single-layer graphene with a very small percentage (less than 5%) of multi-layer domains [18]. Evidence for the growth mechanism of CVD graphene on Cu at low pressure has been provided by Li *et al* using carbon isotope labeling of the CH₄ precursor gas in conjunction with Raman mapping [21]. However, recent studies have demonstrated that the previously observed self-limiting growth of graphene on Cu by low pressure CVD does not apply under all conditions [22, 23, 35–38]. Lee *et al* reported low pressure CVD growth of wafer-scale bilayer graphene films on Cu [22]. They speculate that the key points for the bilayer graphene growth are the depletion of hydrogen,

high vacuum, and, most importantly, slower cooling process ($\sim 18^\circ\text{C min}^{-1}$) compared to previous single-layer graphene synthesis ($40\text{--}300^\circ\text{C min}^{-1}$) [18]. Sample cooling rate has been found to be critical in determining the uniformity and thickness of CVD graphene films on Ni substrates since Ni has high carbon solubility and the segregation of carbon occurs heterogeneously [20]. But when graphene is grown on Cu, the cooling rate has not been expected to affect the quality of graphene films in terms of thickness and uniformity, considering Cu's much lower affinity toward carbon and its surface-catalyzed growth process [21, 38]. Growth of multi-layer graphene on Cu has also been frequently observed under ambient pressure CVD conditions [23, 38]. Bhaviripudi *et al* argued that the reason ambient pressure favors the growth of non-uniform multi-layer graphene is the lowered mass transport rate of active carbon species through the boundary layer (due to steady state gas flow) [35]. A variation in the thickness of the boundary layer can result in thickness non-uniformity of as-grown graphene films. The reduction of carbon precursor supply to ppm levels is needed to deposit uniform single-layer graphene on Cu at such high ambient pressure. Under our ambient pressure CVD conditions, single-layer graphene is produced only at CH₄ concentration as low as 10 ppm (1050C, $1.3\% \text{ H}_2$), while higher CH₄ concentrations ($> 20 \text{ ppm}$) lead to a large number of multi-layer domains.

To further identify and study the multi-layer feature, we grow graphene on Cu foil at a very high CH₄ concentration (500 ppm). Figure 6(a) shows an SEM image of as-synthesized graphene film on Cu; the non-uniform surface contrast in the image indicates the variation of the film thickness. The film can be determined as continuous single-layer graphene with massive multi-layer domains (mostly bilayer, few trilayer). The multi-layer graphene domains can also be identified through contrast differentiation in the optical image (figure 6(b)) of the transferred film on SiO₂/Si substrate. Raman spectroscopy is also used to evaluate the quality and the growth uniformity of the graphene film. Figure 6(c) shows Raman spectra collected from three typical regions in the optical image of the sample (brown background, blue, and dark blue regions in figure 6(b)). All

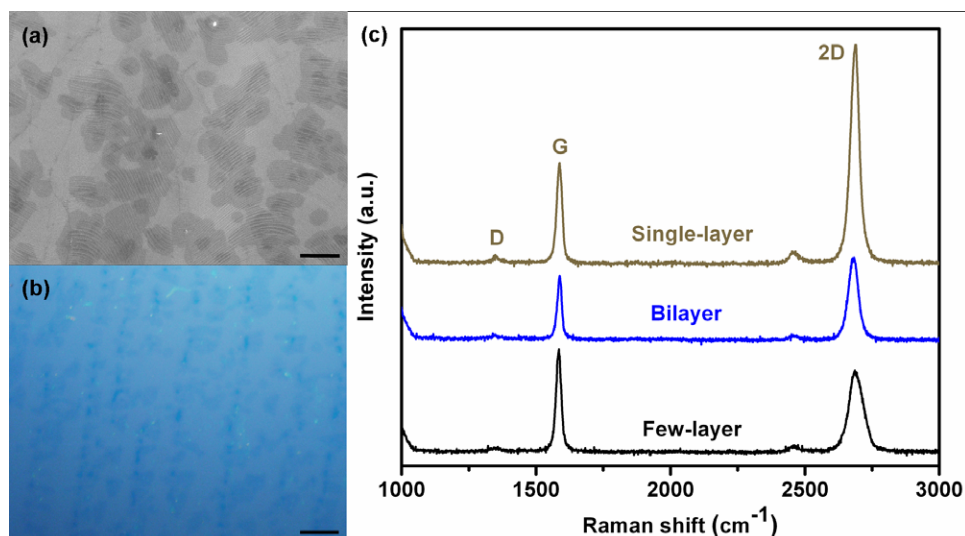


Figure 6. (a) SEM image of CVD graphene grown at high CH_4 concentration (500 ppm) on Cu foil. The scale bar is 10 μm . (b) Optical micrograph of as-synthesized graphene transferred onto SiO_2/Si substrate. The scale bar is 25 μm . (c) Raman spectra (532 nm excitation) of the transferred graphene on SiO_2/Si in image (b) confirming the presence of single-layer (brown background), bilayer (blue regions), and few-layer graphene (dark blue regions).

the spectra show the two primary features of graphene, a G band at $\sim 1587\text{ cm}^{-1}$, and a 2D band at $\sim 2686\text{ cm}^{-1}$. The I_{2D}/I_G intensity ratio of the spectrum from the brown background is ~ 2.2 and the FWHM of its symmetric 2D band is $\sim 32\text{ cm}^{-1}$, indicating that the graphene is single layer. The blue regions with I_{2D}/I_G of ~ 1 correspond to bilayer graphene, and the dark blue regions showing $I_{2D}/I_G < 1$ represent tri- or more layers of graphene. The D band ($\sim 1350\text{ cm}^{-1}$) corresponding to the defect level in graphene from all the spectra is seen to be small, indicating good quality of the film. We also measure the transmittance of the graphene film. It shows $\sim 96.9\%$ at 550 nm wavelength, which implies an average thickness between single-layer ($\sim 97.7\%$) and bilayer ($\sim 95.4\%$) graphene. The sheet resistance of the film is measured to be $\sim 1300\ \Omega/\text{sq}$, much higher even than that of our single-layer graphene sample (produced by two-step ambient pressure CVD). These results suggest that ambient CVD synthesis of graphene on Cu at high CH_4 concentrations can lead to the growth of massive non-uniform multi-layer graphene films, most likely with poor electrical properties.

Understanding of the formation of multi-layer graphene can provide fundamental insight into the growth mechanisms of CVD graphene on Cu. We find that, under CVD conditions with high CH_4 concentrations, nucleation of multi-layer graphene grains is highly preferred, rather than the nucleation of single-layer grains at low CH_4 concentration ($< 10\text{ ppm}$ in our experiments). The formation of multi-layer graphene at the very early stage is a direct result of the excess of supplied active carbon species [23, 39]. We also notice that top layers of the multi-layer domains always have a smaller size than the underlying layers. This can be explained by the very limited supply of active carbon species for the continuous growth of additional graphene layers on the surface of the underlying graphene, since CH_4 molecules stick to and decompose only on a graphene-free Cu surface, producing

carbon adatoms. To better support our view of the formation of multi-layer graphene at an early stage and the limited further growth of the top layers of the multi-layer domains, we first use the two-step CVD technique to grow single-layer graphene on Cu, and then *in situ* apply an extra CVD process (1050°C , 500 ppm CH_4 , 30 min); the as-produced graphene is still a single layer with uniform thickness. The result is also consistent with the point that, once a continuous graphene film forms on the catalytic Cu surface, growth of extra graphene layer is inhibited because of the absence of Cu to catalytically decompose the carbon precursor gas [21].

Based on the above observations and analysis, a simple model can be proposed for the nucleation and growth of graphene on Cu by CVD. The growth process includes four main stages (figure 7): (1) incubation, (2) nucleation and initial growth, (3) growth and coalescence, and (4) formation of films. Depending on CVD parameters, the quality of as-produced graphene films can differ significantly in terms of film thickness, graphene domain size, and film coverage. Figure 7 schematically illustrates the four stages of CVD synthesis of graphene on Cu at 1050°C under two extreme CH_4 concentrations (in our case, 5 and 500 ppm). Cu foil is first reduced and annealed in hydrogen atmosphere to increase Cu grain size and clean the Cu surface. Upon introducing CH_4 at growth temperature, in the incubation stage, the precursor CH_4 is adsorbed on the catalytic Cu surface and decomposed to form active carbon species (C adatoms). Because of the extremely low solubility of carbon in Cu, the formed C adatoms diffuse only on the Cu surface and gradually build up the C adatom concentration. Once a large supersaturation is achieved, spontaneous nucleation and initial growth of graphene grains occur (figure 7(b)). At high CH_4 concentration C adatom concentration increases very rapidly, and a dense nucleation of multi-layer graphene grains is highly preferred, while in the case of low CH_4

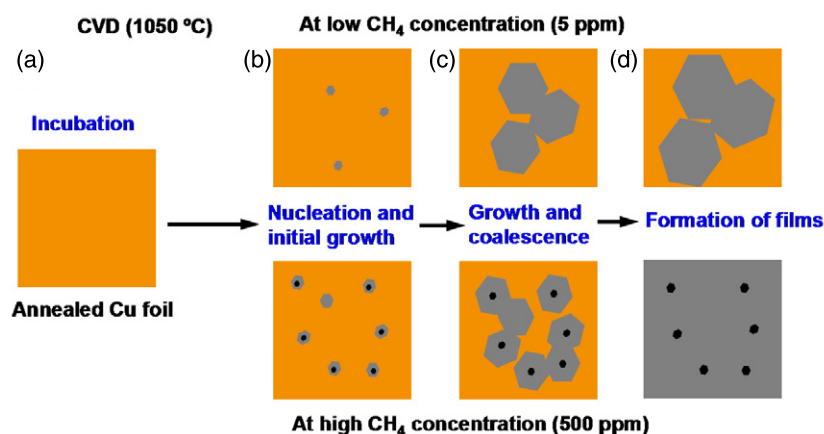


Figure 7. Schematic diagram of growth process of CVD graphene on Cu at low (5 ppm) and high (500 ppm) CH_4 concentrations. Four main stages can be distinguished during growth and highlighted in blue: (a) incubation, (b) nucleation and initial growth, (c) growth and coalescence, and (d) formation of films.

concentration it takes a longer time to reach C adatom supersaturation, and single-layer graphene grains nucleate sparsely. These initial graphene grains continue to grow with time and start coalescing with each other (figure 7(c)), and eventually form graphene films (figure 7(d)). The films are typically polycrystalline, since the initial grains may have different orientations. Graphene grown at high CH_4 concentration is continuous non-uniform multi-layer films with small grain size. On the other hand, single-layer graphene film with large grain size but mostly partial coverage on Cu substrate is obtained at low CH_4 concentration. The partial graphene coverage is because, in the film formation stage, the number of C adatoms available on the exposed Cu surface is insufficient to further drive C attachment to the graphene edges. Equilibrium has been established among graphene grains, the Cu surface, and the carbon vapor phase. In order to break down the equilibrium and form continuous films, a second CVD step can be introduced by simply increasing CH_4 concentration. The proposed two-step CVD process enables the synthesis of continuous single-layer graphene films with large grain size.

4. Conclusions

In summary, we study the graphene nucleation and growth processes on Cu by ambient pressure CVD at a growth temperature of 1050 °C under different CH_4 concentrations, and develop a two-step CVD process to synthesize single-layer graphene films with large domain size. The average grain area can be as large as $\sim 287 \mu\text{m}^2$. SEM and Raman spectroscopy characterizations confirm the film thickness and uniformity. Optical transmittance and sheet resistance measurements, performed on graphene films (up to four layers) transferred on cover glass slips (layer-by-layer transfer), suggest the films' high potential as transparent conductive electrodes. The formation of non-uniform multi-layer graphene films is also discussed, and a growth mode has been proposed for the nucleation and growth of CVD graphene on Cu. Our results provide key insights into the

CVD growth mechanism of graphene on Cu, and may facilitate the synthesis of high quality uniform graphene films and the applications in future nanotechnology.

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