Kinetic study of graphene growth: Temperature perspective on growth rate and film thickness by chemical vapor deposition

Sirui Xing \textsuperscript{a,b}, Wei Wu \textsuperscript{a,b,*}, Yanan Wang \textsuperscript{b}, Jiming Bao \textsuperscript{b}, Shin-Shem Pei \textsuperscript{a,b}

\textsuperscript{a} Center for Advanced Materials, University of Houston, Houston, TX 77204, United States
\textsuperscript{b} Department of Electrical and Computer Engineering, University of Houston, Houston, TX 77204, United States

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We studied graphene growth kinetics from a temperature perspective, particularly the influence on growth rate, nucleation density and film thickness, in the temperature range of 900–1050 °C. The activation energy for graphene growth on Cu is \textasciitilde 2.74 eV. Additionally, bilayer graphene is obtained at 950 °C. Statistics results of the rotation angle suggest that over 75% of the bilayers are twisted graphene while the rest are Bernal (AB)-stacked. Our results provide insight into the optimization of CVD graphene growth on Cu and are beneficial for the development of novel graphene-based electronic devices with tunable characteristics.

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1. Introduction

With the advantages of good quality, scalability, and transferability, graphene films grown by chemical vapor deposition (CVD) on transition metals (e.g., Ni, Cu) have shown high potential for the commercialization of graphene based electronic devices [1–3]. Among these metal substrates, Cu turns out to be the most favorable not only due to its cost efficiency, but also its capability of controlling graphene film thickness [4]. The CVD conditions for graphene growth on Cu have been intensively studied in order to improve the quality, e.g., large single crystal domain size, uniform thickness and controlled doping [5–7]. Bhaviripudi et al. tailored CH\textsubscript{4} concentrations and got uniform monolayer graphene films under both low pressure and ambient pressure CVD processes [8]. By carefully controlling H\textsubscript{2} concentration, Wu et al. reported the growth of single crystal domains of monolayer graphene larger than 0.2 mm, on melted Cu at 1090 °C [9]. Growth temperature has been demonstrated as a critical parameter; however, the detailed effects on graphene growth and film thickness remains fragmentary. In addition, industry would greatly prefer a low temperature graphene growth process for a high cost efficiency. A systematic study on growth kinetics is necessary for a better understanding of the CVD process, as well as for the further improvement of graphene quality.

The CVD growth of graphene on Cu was believed to be a self-limiting process, which enables the formation of predominantly monolayer graphene films [4,10]. This self-limiting effect, however, can be easily broken under ambient-pressure CVD conditions with a high concentration carbon source and/or low growth temperature, and multi-layer graphene grains can nucleate and grow [5,8,11]. Such multi-layer graphene, particularly bilayer, have recently attracted great interest due to the tunable band structures with different stacking arrangements (i.e., rotation angles) between graphene layers [12–14]. Zhang et al. demonstrated a widely tunable bandgap of up to 250 meV in electrically gated AB-stacked (Bernal-stacked) bilayer graphene [15]. A strong rotation-angle dependence of twisted bilayer graphene Raman features (the 2D and G peaks) was reported by Kim et al. from experimental and theoretical studies [16]. Recent experiments have shown that CVD grown graphene bilayers contain both AB-stacked and twisted (0–30°) graphene [17–19].

In this Letter, we report the growth of graphene on Cu by CVD at different temperatures ranging from 900 to 1050 °C, and systematically study the effect of temperature on the growth process, including growth rates, coverage percentage, film thickness and nucleation density. Based on the assumption that growth rate is proportional to the uncovered Cu surface ratio, we derive an exponential equation characterizing the graphene coverage ratio as a function of growth time. Such an equation fits well with our experimental data. Activation energy of \textasciitilde 2.74 eV has also been estimated for graphene growth on Cu. In addition, graphene bilayers are obtained at 950 °C and the interlayer stacking arrangements have been analyzed. Statistical results of the rotation angle distribution indicate that the majority of the graphene bilayers are twisted graphene, of which the Raman spectra largely differ from those of the AB-stacked bilayers. Our studies could not only benefit fundamental research on improvement of graphene quality, but also shed light on development of novel tunable graphene electronics.
2. Experimental methods

2.1. Graphene growth

Graphene was grown on Cu foils (25 μm in thickness, 99.8% Alfa) by ambient pressure CVD of CH4 in a quartz tube furnace at temperatures ranging from 900 to 1050 °C. Before CVD, sequential cleaning of Cu foils in acetone, methanol, and DI water was performed. After cleaning, Cu foils were loaded into the furnace, then reduced and annealed in mixtures of Ar and H2 at 1050 °C for 30 min to minimize Cu surface defects. We fixed the CH4 concentration to 20 ppm balanced in Ar and H2 with the H2 concentration of 1.3%. The growth time ranges from 5 to 60 min. After growth, samples were fast-cooled down to room temperature in Ar and H2.

2.2. Characterization

Graphene samples were wet-transferred onto SiO2/Si substrates for characterization using scanning electron microscopy (SEM, LEO 1525), optical microscopy, and Raman spectroscopy (XploRA, HORIBA). Raman spectra were collected at room temperature with a 532 nm laser. The laser source was focused to a spot of ~1 μm using a 100× objective lens, and the laser power was kept below 2 mW to reduce the thermal effects. The graphene wet-transfer process is the same as previously reported [20,21]. A thin layer of polymethyl methacrylate (PMMA) was used as the supporting material during transfer, and the Cu etchant we used was 0.1 g/ml iron nitrate solution.

3. Results and discussion

In CVD of graphene on Cu, the growth temperature plays a critical role in determining graphene thickness and film coverage. At 1050 °C, individual graphene grains of single-layer thickness are initially grown and eventually merge into a continuous film after 30 min (~98% coverage). As shown in Figure 1(a), the very limited color variation indicates a homogeneous film. By decreasing growth temperature to 1000 °C, graphene bilayer domains appear, as the relatively darker areas in Figure 1(b). The ratio between the size of bilayer region and the size of graphene grain (denote as $R_{B2G}$) is as low as 0.2. When the growth temperature drops to 950 °C, the ratio $R_{B2G}$ increases to ~0.5 (Figure 1(c)). Most grains have bilayer regions up to ~6 μm, and such well-defined hexagonal bilayers were verified to be graphene single crystals [21]. When the growth temperature is further reduced to 900 °C, after 60 min growth, the Cu substrate is partially covered by ~2 μm graphene grains with only ~35% coverage (Figure 1(d)). Two types of grains can be distinguished in this case: monolayer hexagons and few-layer grains. Judged by their irregular shape, the thicker regions of the few-layer grains (inset in Figure 1(d)) are not in a good crystalline nature [5,11]. When the temperature decreasing below 850 °C, graphene can hardly be grown even after 60 min duration. Our results suggest that the formation of bilayer or few-layer graphene is highly preferred at relatively low growth temperatures (900–1000 °C). The phenomenon of such temperature-dependent graphene thickness can be explained as follows: The decomposition of methane leads to supersaturation of active carbon species (e.g., C adatoms) at the Cu surface. When the C concentration reaches a critical point ($C_{nuc}$), graphene nucleation occurs and C concentration drops to a normal growth level ($C_{growth}$) [22–24]. The difference (ΔC) between $C_{nuc}$ and $C_{growth}$ is the amount of C consumed during nucleation. We believe, at lower temperatures, both $C_{nuc}$ and $C_{growth}$ drop, but the difference ΔC increases compared to that of high temperatures. Such increased amount of C contributes to multi-layer nucleation. Since $C_{growth}$ drops at low temperatures, the growth rate decreases accordingly. As a consequence, more CH4 (i.e., higher concentration) is required to achieve the growth of continuous and even thicker graphene films [7,19].

Graphene formation begins with CH4 decomposition, which is a surface catalysis process. We apply the kinetic model under the assumption that growth rate (graphene coverage rate, noted as $V_{coverage}$) is proportional to the uncovered Cu surface ratio: $V_{coverage} = \frac{dC_{coverage}}{dt} = \alpha(1 - \text{Coverage})$, where (1 – Coverage) is the fraction of the bare Cu. This indicates a proportional relationship between the graphene coverage rate and the amount of exposed...
Cu surface. Similar relationship has also been reported on other substrates, such as Ru(0001), where graphene is deposited under UHV [23]. The rate is the highest initially, and then it decreases as graphene grows and covers the Cu surface. Eventually, graphene coverage stops increasing when equilibrium has been achieved among graphene, carbon vapor phase, and any exposed Cu surface. By integrating the above equation, we derive the coverage equation

$$\text{Coverage} = \frac{\alpha}{C_0} e^{\frac{t}{\alpha} + 1},$$

where \( t \) is the time and \( \alpha \) is a constant defined by the growth temperature. We find the coverage equation fits well with the experimental data in Figure 2(a), and we calculate \( \alpha \) at different temperatures. As shown in Figure 2(b), \( \alpha \) increases dramatically as temperature increases from 900 to 1050 °C. To further study the growth kinetics of CVD graphene on Cu, we calculate the activation energy for graphene growth using the Arrhenius equation \( \frac{\alpha}{e^{\frac{E_a}{kT}}} = kT \), where \( k \) is the Boltzmann’s constant and \( T \) is the absolute temperature. From the Arrhenius plot shown in Figure 3(a), we obtain an \( E_a \) of ∼2.74 eV. Kim et al. has suggested a wide range of activation energies (1–3 eV) for graphene nucleation and growth on Cu [24]. And our result is comparable to the reported value of ∼1.5 eV for low pressure CVD graphene on Cu found by Colombo et al. [25]. Such an energy barrier may due to the combination effect of methane decomposition, carbon species adsorption and desorption, and graphene cluster formation.

Figure 3(b) shows graphene nucleation densities and grain areas obtained at different temperatures. The nucleation density strongly depends on the growth temperature; it reaches the order of \( 10^6 \) on a centimeter square and drops to \( 10^5 \) as the temperature rises from 900 to 1050 °C. On the other hand, the average grain area increases from ∼6 to ∼225 µm² at 900 °C and 1050 °C, respectively. The results suggest that high temperatures can be applied in CVD of graphene in order to grow graphene films with large crystal grains and low nucleation density [25]. Indeed, with optimized CVD conditions that largely suppress nucleation density, the growth of single crystal graphene domains with areas up to mm² have been reported on melted Cu substrates [9,26].

Of all the growth results at different temperatures, the bilayer graphene grains obtained at 950 °C hold great attraction due to their well-defined hexagonal shape and intriguing interlayer relation. High magnification SEM images of the graphene grains are provided in Figure 4(b–f). The grains have two stacked hexagonal layers with the smaller, darker regions being bilayer, and the two graphene layers, which are either oriented (AB-stacking, verified by Raman in Figure 5) or arranged in a relative rotation (e.g., 29° in Figure 4(f)). Our previous work has demonstrated that the smaller layer of bilayer graphene is actually nucleated and grown next to the substrate below the larger layer [27]. In such “growth from below” process, the buried graphene layer is most certainly grown more slowly than the overlying layer, since it is more difficult for C adatoms to diffuse through the overlying layer to the edges of the buried graphene and contribute to its further growth.

We measured the rotation angles of over 100 our CVD bilayer grains based on SEM images. Relative rotation between the two hexagonal layers can be used to estimate the actual crystallographic orientation in the bilayers [27], since it has been well reported that the edges of CVD graphene grains with hexagonal shapes are parallel to zigzag directions [21,28]. The statistics of the rotation angle distribution is shown in Figure 4(a). The graphene bilayers are more likely (up to ∼15%) to possess an oriented AB-stacking arrangement to achieve the lowest energy state.

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Figure 2. (a) Graphene coverage on Cu as a function of growth time obtained at different temperatures. The individual markers indicate experimental data, and the solid curves represent the exponential fitting of each set of the data at a given temperature. (b) Growth rate \( \alpha \) depends on temperature, indicating how fast the film is growing.

Figure 3. (a) Arrhenius plot of the ln(\( \alpha \)) as a function of 1000/T. The activation energy for the growth of graphene computed from the slope of the linear fitting. (b) Graphene nucleation density and grain size as a function of growth temperature.
[29,30]. There is also a slight preference of ~29° rotated bilayer graphene, although for the rotated graphene multilayers, 27.8° rotation angle has been calculated as a relatively low energy configuration [31,32]. In addition, the bilayers with rotation angles between 0° and 30° can also be frequently observed, suggesting no strong confinement effect from the growth substrate on crystallographic orientation of the two layers of bilayer graphene. This agrees with the finding that the interaction between CVD graphene and the underlying polycrystalline Cu substrate is relatively weak compared to other graphene-metal systems, e.g., graphene on Ru(0001) [33,34]. However, epitaxial growth of graphene has been fulfilled by CVD on single crystal Cu(111), where the graphene lattices are most closely aligned with the Cu(111) lattice [35,36].

The Cu(111) substrate could exert strong influence on both the layers of graphene island, and may be a possible way to get predominantly AB-stacked graphene bilayers. Although it may not be easy to control the stacking arrangements of CVD bilayer graphene precisely, the variety of its rotation angles has been an advantage in studying any new electronic and optical properties of these twisted bilayers [16,18].

We intentionally choose graphene bilayers of 0° and relatively large rotation angles for characterization by Raman spectroscopy to verify the graphene quality and the interlayer stacking. Figure 5(a) and (b) show optical images of individual oriented bilayer grain and twisted grain (~23° rotation) transferred on SiO2/Si, respectively. Their typical Raman spectra are shown in Figure 5(c).
5(c). Raman spectrum of the monolayer region of the bilayer graphene is also recorded as reference (Figure 5(c), black line). For monolayer graphene, G band shows at ~1586 cm\(^{-1}\) and 2D band shows at ~2679 cm\(^{-1}\) with a \(I_{2D}/I_{G}\) intensity ratio of ~2.11. The full width at half-maximum (FWHM) of the 2D band is ~31 cm\(^{-1}\). From the spectrum of the oriented bilayer grain (Figure 5(c), red line), a reduced \(I_{2D}/I_{G}\) intensity ratio of ~0.8 and a broader 2D band at ~2686 cm\(^{-1}\) with a FWHM of ~54 cm\(^{-1}\) are observed. In comparison with the monolayer region, the 2D band of the oriented bilayer grain is blueshifted by 7 cm\(^{-1}\) and its G band at ~1578 cm\(^{-1}\) shows an 8 cm\(^{-1}\) redshift. All these Raman features correspond well to the characteristics of AB-stacked bilayer graphene [37,38]. The Raman spectrum of the ~23° rotated bilayer grain (Figure 5, blue line), however, resembles that of monolayer graphene, with the same 2D band FWHM of ~31 cm\(^{-1}\) and a very similar \(I_{2D}/I_{G}\) intensity ratio of ~2.07. It suggests a weak interlayer coupling in rotated bilayer graphene especially of large rotation angles [16]. Compared to monolayer, the ~23° rotated bilayer 2D band at ~2683 cm\(^{-1}\) and the G band at ~1581 cm\(^{-1}\) are slightly blueshifted of 4 cm\(^{-1}\) and redshifted of 5 cm\(^{-1}\), respectively. The quality of the graphene bilayers can be inferred from the Raman D band (~1342 cm\(^{-1}\), corresponding to defect level in graphene). The absence of the D band in the oriented bilayer grain indicates the high quality of the AB-stacked bilayer graphene, while, the presence of D band shows a relatively high intensity in the ~23° rotated bilayer grain suggesting the existence of disorder-induced defects. It is worth mentioning that we also observe a D band in the monolayer region of the bilayer grains, most likely originating from the grain edges and/or graphene-substrate interactions.

4. Conclusions

In summary, we study the graphene growth kinetics from temperature perspective on Cu by ambient pressure CVD at different growth temperatures ranging from 900 to 1050 °C. The growth of bilayer or few-layer graphene is highly favored at low temperatures, and under optimized CVD conditions, mostly bilayer graphene grains are grown at 950 °C. We also find that the rate at which graphene covers the Cu surface is proportional to the amount of uncovered Cu surface. Activation energy of ~2.74 eV has been derived from the Arrhenius equation. In addition, we analyze the stacking arrangements of the graphene bilayers grown at 950 °C. Statistical results show that over 75% of the bilayers are twisted graphene with a slight preference for ~29° rotation. Raman characterization indicates that the oriented bilayers are AB-stacked bilayer graphene, but the twisted ones show distinguishable Raman features. Our study has contributed to understanding CVD graphene growing mechanism and modeling, paving the way for new applications of twisted bilayer or few-layer graphene.

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