Synchronous Growth of AB-Stacked Bilayer Graphene on Cu by Simply Controlling Hydrogen Pressure in CVD Process

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ABSTRACT

AB-stacked bilayer graphene has attracted considerable attention due to its feasibility of band gap tuning. Although synthesis of bilayer graphene on Cu has been reported using chemical vapor deposition (CVD) through a layer-by-layer growth mechanism, the process is long and complicated due to lack of catalytic assistance of Cu to the second graphene layer growth. Here we show that theoretical modeling demonstrates an alternative synchronous growth of bilayer graphene on Cu is possible by passivating the top graphene nuclei edges with hydrogen to allow carbon diffusion underneath the top graphene nuclei for bottom graphene layer formation. Moreover, such a growth mechanism has been achieved experimentally in a facile CVD method by simply controlling the H₂ pressure. Bilayer graphene with high coverage of over ~95% and a high AB stacking ratio of up to ~90% has been obtained within a short growth time of 30 min. Also, graphene with single, double and multiple layers can be obtained by simply controlling the hydrogen pressure. This result represents the demonstration of the fast synchronous AB-stacked bilayer graphene growth, which is important to scalable manufacture of graphene with controllable layer number and stacking required for practical applications.

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1. Introduction

Bernal-stacked (AB) bilayer graphene, where half of the carbon atoms in the second layer sit on top of the empty centers of carbon hexagons in the first layer, has recently attracted considerable attention because a bandgap of up to 0.25 eV can be induced by exerting a perpendicular electric field [1, 2]. Bilayer graphene obtained from mechanical cleavage of graphite with Scotch tape or ionic graphite intercalation of selected compounds is inherently AB stacked [3, 4]. Although these methods provide the most reliable ways to produce AB-stacked bilayer graphene with high quality, they are not applicable for scalable manufacture of graphene required for practical microelectronic devices and circuits. Chemical vapor deposition (CVD) methods have been recently developed to synthesize AB-stacked bilayer graphene on Cu foil through a layer-by-layer growth mechanism [5-9]. But an immediate difficulty encountered in the layer-by-layer graphene growth is caused by lack of catalytic assistance of Cu after its surface is covered with the first graphene layer, resulting in a longer growth period of several hours for the second layer [5-7]. Bilayer graphene growth can also be achieved by using complicated binary metal alloy catalysts (i.e., Ni-Cu) while at cost of reduced sample uniformity owing to the non-uniform alloy composition [8, 9]. Therefore, it is highly desirable to develop a simple and cost-effective route to fabrication of AB-stacked bilayer graphene of practical significance.

It is well known that H_2 plays an important role in the growth of bilayer graphene in the CVD processes. [10, 11] Very recently, on the basis of density functional theory (DFT) calculations at the ground state, Zhang et al., have suggested an alternative underlayer growth mechanism of bilayer graphene at high hydrogen pressures [12]. In this model, the top-layer graphene nuclei edges are passivated by excessive H and thus could be detached from the Cu surface to allow diffusion of active C species into the area beneath the graphene top layer to form the adlayer graphene underneath [12]. If indeed a balance could be achieved between the top-layer graphene nuclei edge passivation and the bottom graphene adlayer nucleation,

synchronous bilayer graphene growth may be achieved. The unique advantage of this growth mechanism is the availability of the catalytic assistance of Cu to both graphene layers, which could lead to high growth rate for bilayer graphene. Motivated by this, we have simulated the dynamics of a small as well as a moderate size cluster of a monolayer graphene positioned on top of the Cu (111) surface at the typical graphene growth temperature to understand the role of H in affecting the top-layer graphene edge attachment to Cu surface. Through an *ab initio* molecular dynamics (AIMD) simulation, we have especially explored the role of hydrogen in maintaining an opening gap between Cu (111) and C edges by passivating the C edges of the top-layer graphene with H to facilitate nucleation of the bottom graphene layer for bilayer graphene. On the basis of the theoretical calculations, we have carried out a systematic study of graphene growth at 1010 °C as H₂ pressure was varied in a wide range. We found that the AB-stacked bilayer graphene can synchronously grow on Cu within a window of H₂ pressure in low-pressure CVD (LPCVD). Using this LPCVD process, we have experimentally synthesized large and continuous bilayer graphene films on Cu foil with a high coverage (over ~ 95 %) and a high AB stacking ratio of up to 90% within 30 minutes. This method not only significantly simplifies the CVD growth of bilayer graphene, but also provides insights on the graphene nucleation and evolution on Cu through an alternative synchronous growth.

2. Experimental

2.1 Graphene synthesis

A 25 μm thick Cu foil strip was placed at the center of a quartz tube (2.5 cm in diameter) inside a horizontal tube furnace with a down-stream valve was set for a specific pressure. The system was evacuated to a vacuum of 2 mTorr for 10 min, and then 7 sccm H₂ was introduced into the quartz tube. The H₂ pressure was tuned for a specific pressure selected in a wide range of 0.04-30 Torr by the down-stream valve. When the growth temperature reached 1010 °C, 40 sccm CH₄ was introduced to initiate the graphene growth. After 30 min of growth, a continuous graphene film was deposited on the Cu foil strip.

2.2 Graphene Device Fabrication and Measurement

The electrical properties of the bilayer graphene were characterized by fabricating FET devices on 90 nm SiO₂ substrates. Briefly, the bilayer graphene films were transferred onto SiO₂ (90 nm) p-doped silicon substrates. As previously reported,[13] the samples were immersed in acetone afterwards to remove PMMA, which was followed with 400 °C annealing for 30 min in H₂/Ar gas in order to remove residual PMMA. Two-step photolithography processes were carried out to deposit electrodes and pattern the graphene into FETs. As a result, Ti/Au (2/80 nm) source-drain electrodes were deposited by electron beam evaporation and a graphene stripe with 20 μm width and 10 μm length was formed after O₂ plasma etching. For the top-gate fabrication, we employ an ionic liquid of N, N-diethyl-N-(2-methoxyethyl)-N-methylammonium bis-(trifluoromethylsulfonyl)-imide (DEME-TFSI) as the gate dielectric material due to its large electrochemical window, large capacitance and the minimal electrochemical reaction.[14] The electrical transport measurements were performed in vacuum using an Agilent B1505A power device analyzer in a probe station.

3. Results and discussion

The dynamics of a small and a moderate size cluster of a monolayer graphene positioned on top of Cu (111) surface were simulated in the growth temperature window for graphene typically in the range of 1000-1100 °C. The graphene sheet was decorated with hydrogen atoms at the terminating C atoms (Fig. 1a). It should be reasonable to assume that with the presence of excess hydrogen, there will be more likelihood that the C edges of the monolayer graphene bond to hydrogen atoms. For a reference, we also simulated a small cluster of graphene without the presence of hydrogen atoms bonded to the C edges (Fig. 1b). These two cases do not necessarily mimic the experimental conditions, rather they are merely ideal/hypothetical conditions. The main objective here is to see whether or not there is any additional dynamic factor that contributes to a possible ease in diffusing C adatoms underneath the top graphene monolayer. For these hypothetical cases, we performed an

AIMD simulation as implemented in VASP code under a constant temperature and volume (NVT) ensemble using the following specifications: (1) The PAW-PBE potentials within the generalized gradient approximation (GGA), i.e., Cu, C and H; (2) the normal precision with an additional electronic convergence criterion set at 10^{-4} eV with an energy cutoff of 450 eV; (3) an MD time step of 2 fs each with a total simulation time up to 2 ps; and (4) the gamma-point only calculations. [15-17]

Fig. 1 AIMD simulation trajectory results of a small graphene cluster (24 C atoms) on top of a (111) Cu slab (144 atoms). (a-b) Initial set ($t=0$) of two identical monolayer graphene (a) with and (b) without the hydrogen atoms passivation. (c-d) The atomic configuration after 0.5 ps of simulation showing (c) the anchorage of graphene edges onto the Cu (111) surface due to the Cu-C directional bonding and (d) the retention of a layer distance between graphene and Cu (111) surface due to the presence of hydrogen atoms. (e-f) A closer look at the small graphene cluster (e) without and (f) with hydrogen atoms decorating the edges. Note the large gap opening facilitated by the presence of passivating edges.

Fig. 1c shows the atomic configuration after 0.5 ps of simulation showing the C edges effectively anchored onto the Cu (111) surface due to the Cu-C directional bonding. In contrast, in Fig. 1d, we observed a relatively large gap retained when hydrogen atoms were initially placed on the edges. We should note that some of the hydrogen atoms detach from the graphene layer or form a C_2H_2 gas. The exact role of a partially passivated graphene on the growth mechanism of the bilayer graphene is not clear at the moment, but we do notice once the hydrogen atoms are detached from the C edges, these edges become more likely to anchor onto the Cu (111) consistent with our similar observation of H-free graphene cluster. Interestingly, we also observed that a larger inflection of the passivated graphene was in fact observed when some of the C edges are no longer passivated and anchored onto the Cu surface instead. Presumably, this is due to the bending initiation of a single sheet graphene which tends to favor defective edges [18]. A closer look at the atomic configurations based on the two cases is shown in Fig. 1e (without H) vs. Fig. 1f (with H). This result suggests that hydrogen could play a crucial role in manipulating the graphene nucleation and evolution on Cu towards synchronous multilayer graphene growth mechanism, instead of layer-by-layer one, by passivating the C edges to open a gap between Cu and C edges to facilitate an underlayer graphene growth [12].

To verify the theoretical predication, an actual growth following the theoretical prediction was carried out experimentally at 1010 °C in LPCVD by using a gas mixture of H_2 (7 sccm) and CH_4 (40 sccm CH_4), with the H_2 pressure varied in the range of 0.04-30 Torr (instrument limit) controlled by a down-stream valve. Fig. 2a shows that a continuous graphene film was deposited on a Cu foil strip after 30 min of growth at H_2 partial pressure of 0.4 Torr. Fig. 2b shows a typical Raman spectrum of the as-synthesized graphene, which shows two characteristic peaks, i.e., the 2D band at 2701 cm^{-1} and the G band at 1581 cm^{-1} . The negligible D band indicates the graphene is largely defect free. The intensity ratio of the 2D band to the G band (I_{2D}/I_G) is ~ 1 , characteristic of the AB-stacked bilayer graphene [6, 9, 19].

The full width at half-maximum (FWHM) of the 2D band is $\sim 56 \text{ cm}^{-1}$ for the AB-stacked bilayer graphene, which is distinctive from that (i.e., $28\text{-}33 \text{ cm}^{-1}$) of the disoriented bilayer or monolayer graphene [5, 9]. Compared to disoriented bilayer or monolayer graphene that has a single sharp 2D band, the 2D band of the AB-stacked bilayer graphene is much broader and consists of four fingerprint sub-peaks ($2D_{1B}$, $2D_{1A}$, $2D_{2A}$ and $2D_{2B}$), two of which, $2D_{1A}$, $2D_{2A}$, have high relative intensities than the other two, as shown in Fig. 2c [6-9, 20]. In Fig. 2d, the average I_{2D}/I_G values in the range of 0.9-1.3 and FWHM in the range of $49\text{-}62 \text{ cm}^{-1}$ have been calculated as function of the locations, suggesting a highly uniform AB-stacked bilayer graphene across the length of the Cu strip.

Fig. 2 (a) Photograph and (b) Raman spectrum (488 nm excitation) of a representative AB-stacked bilayer graphene on a Cu foil grown at H_2 partial pressure of 0.4 Torr. (c) Peak fitting of the 2D peak (b, baseline subtracted). (d) Statistics of the average I_{2D}/I_G and FWHM of the graphene on the Cu strip.

Fig.3 (a) Optical microscopic and Raman mapping images of the (b) G, (c) 2D, (d) G and I_{2D}/I_G ratio of the AB-stacked bilayer graphene transferred on SiO₂ (90 nm)/Si, respectively. (e) Raman spectra from the marked spots with corresponding colored circles.

Raman mapping images were also collected to further demonstrate the high quality and uniformity of the as-synthesized bilayer graphene transferred on a SiO₂(90nm)/Si substrate. Fig. 3a shows an optical microscopic image of the bilayer graphene with high uniformity transferred on the SiO₂/Si. The G, 2D and I_{2D}/I_G (~1) Raman mapping images (Fig. 3b-d) confirm the bilayer graphene with a high coverage of over 95 % and a high AB stacking ratio up to ~90 %.

Moreover, atomic force microscopy (AFM) was also used to characterize the same graphene film, which has a thickness of ~1 nm (Fig. 4a), characteristic of a bilayer graphene [21]. Fig. 4b shows a graphene film transferred on a glass substrate. The average

transmittance of the graphene at 550 nm is ~94.2 %, which also confirms that the graphene is predominantly bilayer [22, 23].

Fig.4 (a) A typical AFM image of the bilayer graphene film transferred on a Si substrate. Height profile taken along the blue line on graphene shows an average thickness of ~1 nm. (b) Transmittance of the bilayer graphene film transferred onto a glass substrate. Inset in (b) is a typical Raman spectrum of bilayer graphene on the glass substrate.

It should be pointed out that although the CH₄ flow may exert an influence on the resulting graphene [24-26], H₂ is a key factor to break the self-limit effect of graphene growth on Cu foil to enable the layer-by-layer epitaxy growth of bilayer graphene, which has been verified both theoretically and experimentally [5, 12]. To shed some light on the role of H₂ pressure in breaking the self-limit effect of Cu, the graphene growth was repeated while the H₂ pressure was systematically varied in the range of 0.04-30 Torr. Fig. 5a shows Raman spectra of the graphene grown under different H₂ pressures. Fig. 5b presents the changes of the average I_{2D}/I_G of the graphene with the H₂ partial pressure. The growth of bilayer graphene predominates with I_{2D}/I_G of ~1 when the H₂ partial pressure ranges from 0.2 to 3 Torr (purple shaded). Below this range, monolayer graphene was obtained as evidenced from the I_{2D}/I_G ratio up to 3.2 at the lower limit of pink shaded pressure range, while above this range (grey shaded), the I_{2D}/I_G decreases monotonically to <1 with increasing H₂ pressure, indicating a

transition to multilayer graphene growth, both cases of which are in agreement with previous results.[11, 27]

Owing to the poor carbon solubility (<0.001 at. %) of Cu, the LPCVD growth of graphene on Cu foil is normally controlled by a self-limited process: the formation of a continuous monolayer of graphene on its surface would passivate the catalytic activity of Cu and thus prevent the formation of the second layer of graphene. In our experiments, when the H_2 partial pressure is no larger than 0.1 Torr, a continuous monolayer graphene film is always formed on the Cu foil after 30 min of growth. At this condition, additional nucleation and growth of graphene on top of the first graphene layer is negligible even when the growth time was extended by three times. This explains the difficulties encountered in CVD bilayer graphene growth on Cu via layer-by-layer mechanism reported previously, which have to involve a long time of (i.e., several hours) growth process due to absence of catalytic assistance of Cu during the second graphene layer growth [5-7].

Fig. 5 (a) Raman spectra of the graphene grown under different H_2 partial pressures. (b) Dependence of the I_{2D}/I_G of the graphene on the H_2 partial pressure. (c) Schematic illustration of the monolayer, bilayer, and few-layer graphene grown on Cu foil.

In stark contrast, our method follows a synchronous-growth mechanism. Fig.5c shows the growth-mechanism scheme of monolayer, bilayer and few-layer graphene grown on Cu foil at different H_2 partial pressure. As a consequence of the synchronous growth, a comparable

growth time is anticipated to achieve a uniform continuous layer of graphene, irrespective of the layer number. This is exactly what was observed in this experiment with the same growth time of 30 minutes for continuous bilayer and multi-layer graphene films. For example, a continuous bilayer graphene film can be formed on the Cu foil after 30 min of growth (Fig.6); but if the graphene growth was quenched after 5 min by quick cooling to ambient conditions, the discontinuous bilayer graphene was formed on Cu (Fig. 7), suggesting that the bilayer graphene initiates from bilayer graphene nuclei and indeed grows synchronously into a continuous film on Cu.

Fig. 6 Two-dimensional (a) I_G , (b) I_{2D} and (c) I_{2D}/I_G Raman mapping of the bilayer graphene film on Cu foil after 30 min growth time, (d) Raman spectra from the marked spots with corresponding colored circles.

Fig. 7 Two-dimensional (a) D, (b) G, (c) 2D, (d) I_{2D}/I_G and (e) I_{2D}/I_G Raman mapping and typical (f) Raman spectrum of the bilayer graphene on Cu at 1010 °C with a mixed H_2/CH_4 flow (7 sccm /40 sccm) after a growth time of 5 min under 0.4 Torr H_2 partial pressure in the synthetic system. (f) Raman spectra from the marked spots with corresponding colored circles.

The electronic properties of the AB-stacked bilayer graphene were also evaluated from the back-gated field-effect transistors (FETs) and dual-gate FETs by transferring the bilayer graphene film onto $SiO_2(90\text{ nm})/Si$ substrates. Fig. 8a shows source-drain current (I_{ds}) versus gate voltage (V_{bg}) under different source-drain voltage (V_{ds}), which indicates an n-type behavior for the bilayer graphene. Such n-type behavior with the neutrality point (V_{gsmin}) at $\sim -5.1\text{ V}$ was consistently observed for FET devices based on the bilayer graphene [9, 28]. In order to extract the mobility of the AB-stacked bilayer graphene, the transfer characteristic

curves were fitted by equations (1) and (2) [29], where V_{Dirac} is the Dirac point voltage, n_0 and n are the carrier densities originated from impurities and back-gate bias, respectively, e is the electron charge, C_{ox} is the capacitance of back-gate oxide, R_{total} is the total resistance of the device consisting of contact resistance R_{contact} and graphene resistance, L and W are the channel length and width, respectively.

$$V_{bg} - V_{\text{dirac}} = \frac{ne}{C_{ox}} \quad (1)$$

$$R_{\text{total}} = R_{\text{contact}} + \frac{L}{W} \frac{1}{e\mu_{\text{FET}}\sqrt{n_0^2 + n^2}} \quad (2)$$

The fitting curves are plotted in Fig. 8b. The hole and electron mobilities of the bilayer graphene have comparable values in the range of $400\text{-}480 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, consistent to those of previously-reported bilayer graphene [6, 21, 30].

Fig. 8 (a) $I_{\text{ds}}\text{-}V_{\text{bg}}$ transfer characteristics at different V_{ds} and (b) the total resistance R_{total} vs V_{bg} curves at $V_{\text{ds}} = 500$ mV for the FET under vacuum at room temperature. (c) R_{total} vs V_{tg} curves at different fixed V_{bg} and (d) top gate voltage V_{tg} vs V_{bg} at the neutral points for the dual-gate FET. Inset in (c) shows the on-off ratio as a function of V_{bg} .

A semiconductor has a bandgap that enables the insulating ‘off’ state (or zero state) in a logic device. A high on/off ratio at room temperature is a key to high-performance electronics. However, single-layer graphene is a zero-gap semiconductor, which lacks the on/off feature. It is worth noting that theory and experiment have confirmed that a bandgap could be induced on a bilayer graphene by applying an external gate electric field [1, 31]. Generally, the bandgap in the bilayer graphene has a linear dependence on the carrier density at ~ 10 meV per addition of carrier density of $\sim 10^{12} \text{ cm}^{-2}$. Fig. 8c shows the maximum resistance at the charge neutral points changes significantly with the back-gate voltage, consistent with the dual-gate behavior of AB-bilayer graphene [3, 32]. The on/off ratio was extracted from the current vs. top-gate voltage ($I_{\text{ds}}-V_{\text{tg}}$) curves under various V_{tg} (in an inset of Fig.8c). The on/off ratio first decreases with V_{bg} changing from -5 to 20 V, then it gradually become slow with increasing V_{bg} from 20 to 40 V. This indicates that the bandgap of bilayer graphene can be adjusted by collaborative back and top voltage. The change of the maximum resistance at different charge neutral points is attributed to the change of vertical field-induced band gap. The fitting line for V_{tg} vs V_{bg} at the maximum resistance (Fig. 8d) has a slope of -0.047. By a linear relation of $-0.047 = \varepsilon_{\text{bg}} d_{\text{tg}} / \varepsilon_{\text{tg}} d_{\text{bg}}$, the dielectric constant (ε_{tg}) of iron liquid top gate can be calculated to be 1.0-2.0, where $\varepsilon_{\text{bg}} = 3.9$ and $d_{\text{bg}} = 90$ nm for the dielectric constant and the thickness of back-gate SiO_2 respectively, and $d_{\text{tg}} = 1\text{-}2$ nm (Debye length) is the thickness of top gate according to electrical double layers model. In addition, the R - V_{tg} curves showed a typical on-off ratio of ~ 3 at $V_{\text{bg}}=0$ V and $V_{\text{ds}} = 20$ mV, which is similar to that in the bilayer graphene obtained by mechanical exfoliation [1, 5].

4. Conclusions

We have demonstrated a facile LPCVD method for synthesis of large AB-stacked bilayer graphene on Cu through a synchronous mechanism proposed originally in theory. Different from the layer-by-layer growth mechanism, the AB-stacked bilayer graphene is initiated from

bilayer graphene nuclei that evolve into a continuous film on Cu within the same growth time as in the monolayer graphene case. The AIMD simulation confirms the critical role of H in affecting the graphene growth by passivating the C edges to reduce the affinity of graphene edges to Cu and allow C diffusion underneath the top-layer graphene nuclei to form the bottom graphene layer with catalytic assistance of Cu. The demonstrated synchronous bilayer graphene growth is important to large-scale applications of graphene in electronics.

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