Controllable and Rapid Synthesis of High-Quality and Large-Area Bernal Stacked Bilayer Graphene Using Chemical Vapor Deposition

Wei Liu,† Stephan Kraemer,‡ Deblina Sarkar,† Hong Li,† Pulickel M. Ajayan,§ and Kaustav Banerjee*†

†Department of Electrical and Computer Engineering and ‡Department of Materials Science and Engineering, University of California, Santa Barbara, California 93106, United States
§Department of Mechanical Engineering & Materials Science, Rice University, Houston, Texas 77005, United States

ABSTRACT: Bilayer graphene has attracted wide attention due to its unique band structure and bandgap tunability under specific (Bernal or AB) stacking order. However, it remains challenging to tailor the stacking order and to simultaneously produce large-scale and high-quality bilayer graphene. This work introduces a fast and reliable method of growing high-quality Bernal stacked large-area (>3 in. × 3 in.) bilayer graphene film or trilayer graphene domains (30 µm × 30 µm) using chemical vapor deposition (CVD) on engineered Cu–Ni alloy catalyst films. The AB stacking order is evaluated by Raman spectra, electron diffraction pattern, and dual gate field-effect-transistor (FET) measurements, and a near-perfect AB stacked bilayer graphene coverage (>98%) is obtained. The synthesized bilayer and trilayer graphene with Bernal stacking exhibit electron mobility as high as 3450 cm²/(V·s) and 1500 cm²/(V·s), respectively, indicating comparable quality with respect to exfoliated bilayer and trilayer graphene. The record high (for CVD bilayer graphene) ON to OFF current ratios (up to 15) obtained for a large number (>50) of dual-gated FETs fabricated at random across the large-area bilayer graphene film also corroborates the success of our synthesis technique. Moreover, through catalyst engineering, growth optimization, and element analysis of catalyst, it is shown that achieving surface catalytic graphene growth mode and precise control of surface carbon concentration are key factors determining the growth of high quality and large area Bernal stacked bilayer graphene on Cu–Ni alloy. This discovery can not only open up new vistas for large-scale electronic and photonic device applications of graphene but also facilitate exploration of novel heterostructures formed with emerging beyond graphene two-dimensional atomic crystals.

KEYWORDS: bilayer graphene, AB stacked graphene, chemical vapor deposition, Cu–Ni alloy, surface catalytic growth

INTRODUCTION

Graphene, the first stable and thinnest two-dimensional (2D) material, which consists of a single layer of sp²-hybridized carbon atoms, has attracted wide interest due to its outstanding electrical and thermal properties and promising applications as electronic and photonic devices;¹−⁴ however, many of those applications are significantly restricted by the zero band gap of graphene⁵ arising due to the inherent symmetry in its structure. Hence, opening a band gap in graphene has become an extremely important topic in the field of graphene nanoelectronics.⁶−¹⁰ In such circumstances, various methods have been explored to open a bandgap in graphene, through physical confinement of the carriers such as by patterning graphene into graphene nanoribbons (GNRs)⁶ and unzipping carbon nanotubes (CNTs) into GNRs.¹¹,¹² However, those methods remain challenging either due to lack of control of the width and edge roughness of GNRs or precisely aligning CNTs on the substrate. Alternatively, Bernal (AB) stacked bilayer graphene can exhibit a bandgap if the symmetry of the electron wave functions in the direction perpendicular to the bilayer can be broken by inducing a potential difference between the two adjacent layers. In fact, bandgap of up to 0.25 eV can be induced when an electric displacement field is built up between the graphene layers by applying a perpendicular electric field, which has been proven by theory and experiments.⁹,¹³,¹⁴ Thus, this bandgap tunability property provides a great opportunity for bilayer graphene to be widely used in electronic and photonic devices. Moreover, the transferability of such graphene layers to any desired substrate made of other 2D nanomaterials with a wide range of bandgaps, such as h-BN (∼5 eV) and transition metal dichalcogenides including MoS₂ and WSe₂ (1.1–2.2 eV), can be exploited to build unique heterostructure devices. In addition, high-transmittance, high-conductivity, and high-flexibility as well as impermeability to moisture (leading to improved reliability) make few layer (2–3 layer) graphene a promising electrode material for a variety of transparent conductor applications.

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Until recently, the most reliable way to produce AB stacked bilayer graphene is exfoliation of natural graphite, Highly Ordered Pyrolytic Graphite (HOPG), or ionic graphite intercalation compounds that are inherently AB stacked, by micromechanical method or sonication method. However, these methods are not applicable for scalable manufacturing of microelectronic devices and circuits. Therefore, it is particularly important to develop a scalable synthesis method such as CVD method that could effectively control the number of graphene layers as well as the stacking order, to enable large-scale production of AB stacked bilayer graphene. Recently, bilayer and few layer graphene growth have been demonstrated on transition metals, such as Ni and Cu, using the CVD method. However, few layer graphene grown on Nist16,17 by CVD tends to be disordered, whereas graphene layers are randomly rotated. Cu has also shown the capability of growing bilayer and few layer graphene domains under certain growth conditions. However, several works have shown that only part of the synthesized bilayer or few layer graphene on pure Cu exhibit AB stacking order. In fact, it is difficult to provide sufficient carbon atoms for uniform few layer graphene growth on pure Cu surface because of Cu’s weak capability of decomposing hydrocarbons. Therefore, bilayer graphene growth on Cu needs a very complicated process and a long growth time (several hours), which are not suitable for large scale production. Hence, creating a reliable and fast method to synthesize large-scale and high-quality AB stacked bilayer graphene by general CVD technique in a controllable manner remains a critical obstacle in developing electronic applications of graphene. Recently, binary metal alloy catalysts such as Cu–Ni2,7–9 have shown high capability in controlling the number of graphene layers. The Cu–Ni alloy system has been widely studied showing that the Cu/Ni ratio at the metal surface can be tuned by varying the bulk Cu/Ni ratio or annealing temperature, indicating the possibility of tuning the graphene growth on the Cu–Ni surface. It is well-known that the stacking order of few layer graphene growing from a carbon precipitation process is non-AB. Therefore, it is important to avoid the carbon segregation process for achieving AB stacked graphene growth. Importantly, in the Cu–Ni alloy system, Cu atoms tend to segregate to the topmost few atomic layers, forming a Cu rich surface. This Cu rich topmost surface could greatly suppress carbon solubility and the segregation process leading to the possibility of controlling the stacking order of a few layers of graphene. Hence, all of the above facts indicate that the stacking order of graphene could be tuned by engineering the Cu–Ni stoichiometry under certain growth conditions (Figure 1a).

Here, we report a versatile CVD graphene synthesis technique employing a stoichiometry engineered Cu–Ni catalyst system, which can grow large-scale high-quality AB stacked bilayer graphene with high probability in a few minutes. Our study also establishes that the surface catalytic effect is the main mechanism for AB stacked bilayer graphene growth on Cu–Ni, which is confirmed by the catalyst component analysis and temperature dependent graphene growth. The method we have developed is the first one that is capable of synthesizing large area Bernal stacked bilayer and trilayer graphene in a fast and controllable manner, which is necessary for large scale production.

Figure 1. (a) Schematic of catalyst engineered graphene growth process on Cu–Ni alloy via surface catalytic mode by suppressing carbon precipitation. The yellow region at the top of the Cu–Ni layer indicates the concentration gradient of Cu. (b) Digital images of Cu–Ni (1200/400 nm) film before (left) and after (right) graphene growth. (c) XRD spectra of the Cu–Ni catalyst after graphene growth. The peaks shown in (c) indicate that Cu-Ni alloy is formed after annealing and graphene growth process. (d) SEM image of graphene grown simultaneously on Cu–Ni alloy (left) and high purity Cu (right), taken from the green circle area in (b). (e) Digital images of monolayer (left) and bilayer (right) graphene on quartz plates. Bilayer graphene is obtained under a different growth condition as shown in Figure 2. (f) Time dependent graphene growth (with corresponding Raman spectra) on Cu–Ni (1200/400 nm) film, graphene growth condition is 920 °C, 0.5 mbar, and 1 sccm CH4/5 sccm H2 for 2, 10, and 30 min. Monolayer graphene covers the Cu–Ni alloy surface in 2 min, and increasing the growth time beyond that still yields monolayer graphene.
monolayer graphene.20 Figure 1e displays the digital images of the adjacent pure Cu area. This difference in the contrast indicates that the number of graphene layers grown on the Cu–Ni alloy is larger than one because high purity Cu (99.999%) films (Figure 1b, left) formed side by side on the same substrate are studied at first to compare their capabilities of graphene growth. Graphene growth was carried out at the optimal conditions for bilayer graphene growth mechanism on Cu–Ni alloy surface. (f, g) 0.2 mbar, 5 sccm H2 for 120 s with 8 sccm CH4 and 10 sccm CH4, respectively. Scale bar is 30 μm for (f) to (g). (h) Optical image of the contiguous area between two bilayer graphene domains. Scale bar is 20 μm for (h). (i) Raman mapping of 2D peak intensity of the contiguous area taken in the white circle in (h). (j) Digital image of bilayer graphene on 300 nm SiO2/Si, the size of the graphene is around 3 in. × 3 in. Raman measurements were performed with a Horiba JY Aramis Raman Microscope system using the 632 nm laser as the excitation source. The spectra were measured in the backscattering configuration using a 100X objective and a 600 grooves/mm grating.

**EXPERIMENTAL SECTION**

Through graphene growth optimization, we found that Cu–Ni with a ratio of 1200/400 nm (1200 nm Cu film was deposited on top of 400 nm Ni) is the best catalyst for AB stacked bilayer growth. In this work, all of the characterizations were carried out on the samples grown on 1200/400 nm Cu–Ni under the optimal growth conditions as shown in Supporting Information S1. Cu–Ni and high purity Cu (99.999%) films (Figure 1b, left) formed side by side on the same substrate are studied at first to compare their capabilities of graphene growth. Graphene growth was carried out at the optimal conditions for bilayer graphene growth as described in Supporting Information Figure S1b. We also deposited Cu–Ni film with fixed Cu/Ni ratio (3:1) using commercial Cu–Ni alloy target and obtained identical graphene growth results with respect to the deposited Cu–Ni film (Cu film deposited on top of Ni). In this study we only discuss graphene growth results using deposited Cu–Ni film as catalyst. Figure 1d shows the SEM image of the boundary area between the Cu–Ni and Cu films after graphene growth under the same growth conditions. It clearly shows that the contrast of the Cu–Ni area is darker than that of the adjacent pure Cu area. This difference in the contrast indicates that the number of graphene layers grown on the Cu–Ni alloy is larger than one because high purity Cu (99.999%) films tend to grow monolayer graphene.20 Figure 1e displays the digital images of the transferred graphene on quartz plates, which are grown on Cu–Ni (1200/400 nm) film (right) and high purity Cu foil (99.999%) (left) under the same growth conditions. The difference in optical contrasts is obvious and agrees with the results of the transmittance measurements (Supporting Information S2). The measured transmittance of the graphene grown on Cu–Ni (1200/400 nm) film is 94% at 550 nm wavelength, in agreement with the reported value for bilayer graphene.21 This transmittance value is lower than that of the monolayer graphene (97% transmittance at 550 nm wavelength measured on a sample grown on pure Cu foil). Hence, Cu–Ni alloy has a higher capability to decompose methane than Cu under the same growth conditions.

**RESULTS AND DISCUSSION**

Contrary to Cu that is known to exhibit weak capability of decomposing methane, Cu–Ni alloy can easily decompose hydrocarbons and provide sufficient carbon atoms on the catalyst surface, leading to the growth of graphene within a short time. Cu–Ni alloy can be covered by monolayer graphene in a short time (less than 20 s as shown in the Supporting Information S3). Once the surface of Cu–Ni alloy is covered by graphene, graphene growth will be terminated because methane cannot decompose on top of graphene. Usually, monolayer graphene can cover the entire surface of Cu–Ni alloy in 2 min (Figure 1f). However, with increase in time, the number of graphene layers on Cu–Ni alloy does not increase any further and only monolayer graphene is obtained even after exposure to methane for a long time (30 min). Hence, time dependent growth (Figure 1f) can prove that graphene growth on Cu–Ni alloy surface obeys surface catalytic mode at lower partial pressure of methane (less than 0.003 mbar). The number of graphene layers is primarily determined by the Cu–Ni ratio, growth pressure and methane partial pressure. As mentioned in previous section, graphene growth on Cu–Ni alloy surface obeys the surface catalytic mode at low methane partial pressure. When the flow rate of methane is increased to 8 sccm at 0.5 mbar, 80% of the graphene film is covered by bilayer domains (Figure 2a). However, the size of bilayer domains varies from 5 to 10 μm (Figure 2a) indicating the formation of a large number of nucleation centers on the surface of Cu–Ni alloy. It has been found that it is possible to reduce the density of nucleation centers by decreasing the partial pressure of hydrocarbon.25 After tuning the flow rate of methane to 3 sccm at 0.1 mbar, large bilayer domains (30–60 μm) with low density appear on Cu–Ni alloy surface (as shown in Figure 2b). However, bilayer graphene regions still cannot cover the entire synthesized Cu–Ni substrate indicating that...
there is an insufficient number of carbon atoms available for the second layer growth (Figure 2e). Along with increase in the flow rate of methane (Figure 2b–d), the size of the bilayer domains increase and eventually the Cu–Ni alloy surface is covered by bilayer graphene (Figure 2d). It is interesting to note that after two bilayer domains merge into one film (Figure 2h), there is no structural disorder in the boundary area as shown by the Raman mapping (Figure 2i). This explains why and how the large-area bilayer graphene films obtained using our technique yield high quality as discussed in the subsequent sections. When we further increase the pressure to 0.2 mbar with a methane flow at 8 sccm (Figure 2f), large area trilayer domains begin to appear. However, trilayer regions cannot cover the entire Cu–Ni substrate even with high flow rate of methane (Figure 2g) implying that it is difficult to grow uniform few layer graphene (>2 layer) at low hydrocarbon pressure. Therefore, controlling the density of the nucleation centers by tuning the partial pressure of methane and providing sufficient carbon atoms on the catalyst play key roles in the synthesis of uniform bilayer graphene (Figure 2d).

By tuning the total pressure and partial pressure of methane, we have achieved large area (3 in. × 3 in.) uniform bilayer graphene as shown in Figure 2j. The number of graphene layers and the stacking order are confirmed by randomly selecting ~110 points across the 3 in. × 3 in. graphene and subsequently mapping the Raman spectra as shown in Figure 4 and Supporting Information S5.

One of the unique properties of Cu–Ni alloy is that it has a Cu rich surface, in which the surface Cu concentration is much higher than the bulk Cu concentration in the topmost 3–5 atomic layers (1–2 nm). By tilting the sample in XPS relative to the detector, Cu concentration at the top surface of Cu–Ni alloy (graphene sample is same as in Figure 2d) is measured with an average concentration of 97 atom % in the topmost 3 nm (includes 1 nm graphene on top of Cu–Ni alloy) as shown in Figure 3a. However, Cu concentration of the topmost several atomic layers should be larger than 97 atom % because 97 atom % is the average value of Cu concentration measured by XPS.

Without tilting the sample, Cu concentration is around 72 atom % at a depth of 8–10 nm (XPS measures surface composition to a depth of around 8–10 nm). Then, the graphene and upper layers of Cu–Ni alloy are removed using argon ion milling (detailed information shown in Supporting Information S5). For the first top 3 nm with the sputtering rate of 0.3 nm/cycle, the measured Cu concentration varies from 72 to 66 atom %. However, Cu concentration remains constant at 66 atom % after 3 nm Cu–Ni alloy is removed by argon ion milling, which is consistent with Cu concentration measured by EDAX as shown in Figure 3d along the red line in Figure 3c (cross section TEM image of Cu–Ni alloy).

Note that the deposited Cu–Ni film has an original Cu concentration of 75 atom %; however, the bulk Cu concentration reduces to 65–67 atom % after a long time annealing due to the evaporation of some Cu. Therefore, we can conclude that there is a Cu concentration gradient in the first 2 nm (excluding the 1 nm graphene on top of the catalyst as shown in Figure 3a). Hence, the above experiments have confirmed that this high Cu concentration on the top surface reduces the carbon diffusion into the bulk leading to the growth of uniform bilayer graphene. After graphene growth, the temperature of our CVD system is decreased from 920 to 850 °C in 5 s. It is known that graphene cannot grow on Ni below 850 °C indicating that carbon atoms will stop segregating to the Ni surface below 850 °C. Therefore, this fast cooling rate can freeze any carbon atoms that might have diffused into the Cu/Ni bulk. Carbon composition analysis is performed by XPS C
from the cross section of the Cu
EDAX spectra (Figure 3e) also cannot detect any carbon atoms
beyond the detection limits of XPS) in the Cu
ion milling indicating that there is almost zero carbon (which is
agreement with the XPS measurement (Figure 3b). Therefore,
signal disappears after 3 nm Cu
surface (black solid curve in Figure 3b). However, the carbon
growth on Cu
graphene by oxygen plasma, there is very strong carbon signal
amount of carbon and carbon oxide is left on the Cu
Ni alloy surface (Figure 3b black dashed curve).
After we removed graphene by oxygen plasma, only a tiny
amount of carbon and carbon oxide is left on the Cu–Ni
surface (black solid curve in Figure 3b). However, the carbon
signal disappears after 3 nm Cu–Ni alloy is removed by argon
ion milling indicating that there is almost zero carbon (which is
beyond the detection limits of XPS) in the Cu–Ni alloy bulk.
EDAX spectra (Figure 3e) also cannot detect any carbon atoms
from the cross section of the Cu–Ni alloy, which is also in
agreement with the XPS measurement (Figure 3b). Therefore,
one can conclude that graphene growth on Cu–Ni alloy obeys
the surface catalytic mode, in which graphene grows directly on
the Cu–Ni surface, and there is an extremely small amount that
can diffuse into the Cu–Ni alloy.
After transferring graphene onto the substrate (72 nm
alumina/Si), we could easily recognize the number of graphene
layers as marked in Figure 2b using an optical microscope.
Raman spectra is also utilized to verify the number of layers and
stacking mode of the few layer graphene. With reliable optical
contrast, it is possible to identify and compare the finer
differences in the Raman spectra between the monolayer, AB
stacked bilayer, and non-AB stacked bilayer graphene. Figure 4a
shows the Raman spectra of monolayer graphene, AB stacked
bilayer, and non-AB stacked bilayer graphene. It can be
observed that it is easier to recognize the AB stacked bilayer
graphene among the above three types of graphene by
examining the 2D/G ratio. The 2D/G ratio of our AB stacked
bilayer is 0.3–1.3, which is similar to that observed in epitaxial
AB stacked bilayer graphene.26 It is worthwhile to note that the
2D/G ratio of non-AB stacked bilayer graphene could also be
less than 1.33,34 Hence, it is necessary to analyze the line shape of
2D peaks because the 2D peak of AB stacked bilayer graphene
always consists of four subpeaks, which is the fingerprint of AB stacked bilayer graphene, while non-AB stacked bilayer graphene only has a single sharp peak as shown in Figure 4b. In contrast to non-AB stacked bilayer graphene, 2D peaks of AB stacked bilayer graphene have obvious shoulder peaks (blue line in Figure 4b), which are further confirmed by the peak fitting as shown in Figure 4c. Among 50 samples, only one 2D peak could not be fitted into four subpeaks, indicating non-AB stacking order for that sample. A summary of the Raman spectra of AB stacked bilayer CVD graphene with four typical 2D/G ratios is presented in Figure 4d. The peak fitting for the 2D peaks of AB stacked bilayer graphene with various 2D/G ratios is shown in the Supporting Information S6. For all of our non-AB stacked bilayer graphene regions, the 2D/G ratio is always larger than 2, indicating that the twist angle between two individual layers is larger than ~14–20°, which can be attributed to the growth condition such as pressure35 or catalyst type. On the other hand, our AB stacked graphene also has a wider full width at half-maximum (fwhm) than that of the non-AB stacked case with the same number of layers (Table 1). Therefore, we conclude that 2D/G, fwhm values and line shape of 2D peaks can be employed to estimate the stacking order of our CVD graphene in a simple and reliable manner. The stacking order is further confirmed by selected area electron diffraction (SAED) and electrical measurements, which are analyzed in the next two sections.
The AB stacked bilayer graphene coverage is calculated by
counting the 2D/G ratios, fwhm of Raman spectra, and the line
shape of the 2D peak. The distribution of the 2D/G ratio is
shown in Figure 5a, in which 2D/G ratios are in the range of
0.5–1.3, indicating the signature of AB stacked bilayer

![Figure 4](image-url)

**Figure 4.** (a) Raman spectra of monolayer, non-AB stacked (N-AB) bilayer, and AB stacked bilayer graphene synthesized by CVD. (b) 2D peaks of monolayer, non-AB stacked bilayer, and AB stacked bilayer graphene, which are from (a). (c) Peak fitting of the 2D peak (from (a) blue line) for AB stacked bilayer graphene. (d) Raman spectra of AB stacked bilayer graphene for four typical cases with different 2D/G ratios. 2D peak fitting of these four samples are shown in Supporting Information S6.

| Table 1. Statistical Analysis Results of Raman Spectra of Monolayer, Non-AB Stacked Bilayer, and AB Stacked Bilayer Graphene from ~20 Different Samples |
|-----------------------------------------------|-----------------------------------------------|
| 2D peak | position (cm⁻¹) | width (cm⁻¹) |
| 1L | 2138–2641 | 30–36 |
| 2L (AB) | 2651–2659 | 38–46 |
| 2L (non-AB) | 2653–2658 | 28–33 |
graphene. The fwhm of bilayer graphene is mostly in the range of 38−50 cm⁻¹ (Figure 5a). Hence, combined with the analysis of the line shape of 2D peaks, we conclude that our synthesized AB stacked bilayer graphene has an ∼98% coverage.

Besides Raman spectra, electron diffraction is also an efficient technique to distinguish the stacking order and number of graphene layers. It has been demonstrated that monolayer and few layer graphene (AB stack) has hexagonal diffraction patterns.26,35 However, the ratios of the intensities of {1210} over {11̅10} are significantly different for monolayer, AB stacked bilayer, and trilayer graphene.35 Figure 6a,c shows a single set of hexagonal diffraction patterns, which is different from that of the non-AB stacked bilayer graphene.20

From Figure 6a,c, it is clear that the intensity of the equivalent planes {1210} is much higher than that of the inner six spots, which represent the equivalent planes {11̅10}. By analyzing the line profiles of diffraction patterns shown in Figure 6b,d, the intensity ratios between planes {1210} (outer peaks in Figure 6b, 6d) and {11̅10} (inner peaks in Figure 6b,d) are around 2 and 1.5, respectively. These two values indicate that the diffraction intensities shown in Figure 6b,d correspond to AB stacked bilayer26 and trilayer graphene,35 respectively.

Figure 6e shows the HRTEM image of the bilayer graphene, in which carbon atoms are quite well aligned without any defect over the entire range of the HRTEM image, regardless of the amorphous contaminants that got deposited on graphene during the TEM sample preparation. The AB stack structure is also confirmed by the FFT (inset in Figure 6e) pattern, which has two sets of hexagonal spots without twist, which indicates the AB stacking order.

Besides Raman spectra and electron diffraction, electrical transport measurement is another reliable method to estimate the stacking order of few layer (1−3 layer) graphene. By applying a vertical electrical field to few layer graphene with different stacking modes and numbers of layers, the resistances of graphene exhibit distinct behavior, which can be used to estimate the stacking order of few layer graphene.8 Graphene areas are randomly selected and patterned by electron beam lithography. Over 50 dual gate devices were fabricated (Figure 7a, details of device fabrication and device structure are included in the Supporting Information S7). All measurements were carried out under ambient conditions. Figure 7b shows a two-dimensional contour plot of the resistance of a bilayer graphene device as a function of top and bottom gate voltages, $V_{tg}$ and $V_{bg}$, respectively. The resistance of bilayer graphene is also illustrated in Figure 7c using the plot of $R_{total}$ as a function of $V_{tg}$ for different fixed $V_{bg}$ values. It can be observed that the resistance reaches the maximum value at the largest average displacement fields, which is on the top left and bottom right of Figure 7b, and on the left and right of Figure 7c, respectively. This behavior indicates that our bilayer graphene has an AB stacking order.9,14

The ON/OFF ratio (defined as the ratio of maximum to minimum resistance in the $V_{tg}$ range of −5 to 5 V for a fixed $V_{di}$ and $V_{bg}$ (Figure 7c)) of our bilayer graphene device is around 10−15. We found that the ON/OFF ratio of the bilayer graphene device is strongly influenced by the sample treatments. Before depositing the top dielectric layer, baking the device in high vacuum substantially enhanced the device performance. Without vacuum treatment, the bilayer graphene device shows worse ON/OFF ratio (around 5−6) and the resistance tends to keep increasing at certain $V_{tg}$ and $V_{bg}$ in one direction (Supporting Information S8). For trilayer graphene, the resistance evolution, which is shown in Figure 7d,e, decreases with increasing perpendicular electric field due to an overlap between the conduction and valence bands that can be controlled by an electric field, indicating that this trilayer graphene has ABA stacking order.36
The mobility of the bilayer and trilayer graphene could be calculated using the back gated FET devices as shown in Supporting Information S9. For bilayer and trilayer graphene, the electron mobility is around $2400-3450 \text{ cm}^2/(\text{V} \cdot \text{s})$ and $500-1500 \text{ cm}^2/(\text{V} \cdot \text{s})$, respectively. These values are comparable to those of micromechanically cleaved bilayer and trilayer graphene (1500–4000 cm$^2/(V \cdot s)$),37 higher than that of epitaxially grown bilayer graphene (550 cm$^2/(V \cdot s)$),26 and lower than our previously reported non-AB stacked CVD grown bilayer graphene (5500 cm$^2/(V \cdot s)$).20

We found that the stacking order of the synthesized graphene is strongly influenced by the bulk Cu/Ni ratio and growth temperature. Figure 8a shows the yield of AB stacked graphene as a function of bulk Cu/Ni ratio. With low Cu concentration (less than 30 atom %) in bulk Cu/Ni, the yield of AB stacked graphene is almost zero. Under such conditions, graphene growth behavior is similar to that in Ni (Supporting Information S10), due to the high concentration of Ni, which can decompose much more methane and also dissolve more carbon in the Cu–Ni alloy. Those dissolved carbon atoms will segregate to the surface forming nonuniform few layer graphene layer-by-layer with each new layer formed below the existing layer(s) (as in few layer graphene growth mode on Ni38).

When bulk Cu concentration is in the range of 70–80 atom %, Cu–Ni alloy exhibits high probability of growing AB stacked graphene at 920 °C as shown in Figure 8a. When bulk Cu concentration is in the range of 70–80 atom %, the surface Cu concentration is about 95 atom % as shown in Figure 8a. Moreover, as shown in the previous sections, surface catalytic graphene growth mode has been achieved at high surface Cu concentrations in the low pressure CVD process. This indicates that many nucleation centers must form on the catalyst surface. The formation of the nucleation centers is confirmed by the...
existence of individual bilayer graphene domains as shown in Figure 2a, b. On the other hand, the grown bilayer graphene under surface catalytic mode is all AB stacked (Figure 2d). This implies that the nucleation centers of bilayer graphene must be AB stacked. Subsequently, the carbon atoms diffuse to the edge of the nucleation centers and form a uniform bilayer graphene film, thereby preserving the stacking order.

We also found that the yield of AB stacked bilayer graphene decreases along with the increase of bulk Cu concentration (>80 atom %). At such a high bulk Cu concentration, surface catalytic graphene growth mode still dominates graphene growth on Cu−Ni alloy. However, the result of increasing bulk Cu concentration beyond 80 atom % results in a corresponding increase (>95 atom %) in surface Cu concentration (Figure 8a, red curve), which simultaneously decreases the hydrocarbon decomposition (due to lack of Ni) leading to lower carbon concentration on the Cu−Ni alloy surface.

Besides the Cu/Ni ratio, we also found that temperature can significantly influence the yield of AB stacked graphene (Figure 8b). Cu surface concentration is around 95 atom % for the temperature in the range of 880−980 °C as shown in Supporting Information S11. When the temperature is in the range of 915−930 °C, grown graphene has an AB stacked configuration with yield of around 95−100%.

This high yield can be attributed to the achievement of surface catalytic graphene growth mode with a certain methane decomposition rate. However, when the temperature is above 930 °C, the AB stacked graphene yield gradually decreases from 95% to 20% (at 980 °C). In addition, it is difficult to grow uniform bilayer graphene at high temperatures (>930 °C). This can be explained by the fact that high temperature will help the catalyst to decompose more methane and many more carbon atoms will diffuse into the bulk resulting in carbon segregation and thereby decreasing the yield of AB stacked graphene. Although surface catalytic graphene growth mode still occurs on part of the catalyst surface leading to the growth of some AB stacked graphene, carbon atom segregation mode will gradually dominate the graphene formation mechanism along with increase in the growth temperature. On the other hand, at temperatures less than 900 °C, Cu−Ni alloy tends to grow mostly monolayer graphene with small few-layer domains due to insufficient carbon sources. Thus, the AB stacked few layer graphene yield is low.

Therefore, on the basis of the yield of AB stacked bilayer graphene, for both Cu (or Ni) surface concentration and growth temperature, it can be concluded that achieving surface catalytic graphene growth mode and precise control of the surface carbon concentration determines the formation of uniform large scale AB stacked bilayer graphene. To summarize, the optimal growth condition for AB stacked bilayer graphene on Cu (1200 nm)/Ni (400 nm) is to flow 5 scm H₂ and 8 scm CH₄ at 0.1 mbar and 920 °C for 120 s after an annealing at 20 mbar and 990 °C with 100 scm H₂/150 scm Ar for 30 min.

**CONCLUSIONS**

In conclusion, we have demonstrated a reliable bottom-up method for large-area (3 in. × 3 in.) and high quality AB stacked bilayer graphene growth by engineering a bifunctional substrate where the decomposition of hydrocarbons and the surface diffusion induced growth are both tailored with the right combination of surface Cu concentration and temperature. It was found that achieving surface catalytic graphene growth mode and precise control of the surface carbon concentration are key factors determining the favorable growth kinetics for AB stacked bilayer graphene. After catalyst engineering and growth parameter optimization, highly uniform AB stacked bilayer graphene or trilayer domains (30 μm × 30 μm) can be grown on deposited Cu−Ni (1200/400 nm) film on the wafer scale. The AB stacking order of synthesized graphene was confirmed by Raman spectra, TEM diffraction pattern, and dual gated FET measurements. The measured mobility of the bilayer and trilayer graphene was extracted to be as high as 3450 cm²/(V·s) and 1500 cm²/(V·s), respectively, indicating comparable quality with respect to exfoliated bilayer and trilayer AB stacked graphene. Moreover, we demonstrated a large number (>50) of dual-gated field-effect transistors with record high ON to OFF current ratios (as high as 15) fabricated at random across the large-area bilayer CVD graphene film, which further confirms the quality of our synthesized graphene.

**ASSOCIATED CONTENT**

3 Supporting Information

- (1) CVD system setup, growth parameters, and graphene transfer process;
- (2) transmittance of monolayer and bilayer graphene;
- (3) time dependent graphene growth on Cu−Ni film, Cu foil and Ni film;
- (4) Raman spectra of AB stacked and non-AB stacked bilayer and trilayer graphene;
- (5) XPS analysis of Cu−Ni and carbon composition in Cu−Ni alloy;
- (6) 2D peak fitting of AB stacked bilayer graphene;
- (7) dual-gate graphene FET fabrication process flow;
- (8) effect of doping on the performance of bilayer graphene FET;
- (9) mobility calculation;
- (10) graphene growth on Ni rich and Cu rich alloy; and
- (11) calculation of the Cu concentration on surface of Cu−Ni film.

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**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: kaustav@ece.ucsb.edu.*

**Author Contributions**

The manuscript was written through contributions of all authors.

**Notes**

The authors declare no competing financial interest.

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