Synthesis of high-quality monolayer and bilayer graphene on copper using chemical vapor deposition

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ABSTRACT

The mechanisms determining the growth of high-quality monolayer and bilayer graphene on Cu using chemical vapor deposition (CVD) were investigated. It is shown that graphene growth on Cu is not only determined by the process parameters during growth, but also substantially influenced by the quality of Cu substrate and how the Cu substrate is pretreated. It is found that the micro-topography of the Cu surface strongly affects the uniformity of grown graphene while the purity of the Cu film determines the number of synthesized graphene layers at low pressure conditions. On the other hand, a minimum partial pressure of hydrocarbon is required for graphene to cover the Cu surface during graphene growth. The optimized bilayer graphene exhibits a maximum hole (electron) mobility of 5500 cm²V⁻¹s⁻¹ (3900 cm²V⁻¹s⁻¹). A new growth mode resulting in tetragonal shaped graphene domain, which is different from the known lobe structure (for monolayer) or hexagonal (for few layer) mode, is also discovered under our experimental conditions. Furthermore, high resolution transmission electron microscopy has revealed the non-ideal nature of CVD graphene structure for the first time, indicating an important cause of electron/hole mobility degradation that is typically observed in CVD graphene. This observation could be crucial for optimization of the CVD process to further improve the quality of graphene.

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1. Introduction

Graphene, a single atomic layer of carbon atoms arranged in a hexagonal network, has attracted significant attention due to its unusually high carrier mobility and unique band structure [1-3]. The synthesis of large-area high-quality graphene is very important for the high-volume manufacturing of electronic devices. Recently, different methods have been demonstrated for the formation of graphene, such as mechanical exfoliation of graphite [1], sublimation of epitaxial SiC [4], and catalyst-assisted chemical vapor deposition (CVD) [5-9]. However, mechanical exfoliation of graphite can only supply small-size graphene (see Fig. 1), which makes it less efficient and not scalable to high-volume manufacturing. Although sublimation of SiC is a wafer-scale method, SiC substrate is expensive and sublimation of SiC requires very high-temperatures (>1500 °C) [4]. On the other hand, CVD method [5-9], which uses Cu or nickel as catalyst, has been proposed as a promising approach offering higher efficiency and scalability. In particular, the use of Cu film as a catalyst has been successfully demonstrated for the growth of monolayer graphene [9,10], showing great potential for synthesizing large-scale graphene for device applications. However, a key challenge for CVD graphene growth is that their quality (carrier mobility) is much lower than that of graphene obtained via exfoliation of graphite as summarized in Fig. 1.

While many efforts have been spent on investigating the growth mechanism of CVD graphene on Cu as well as on the techniques for improving the uniformity and quality of graphene [11-14], there is still a lack of comprehensive

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A 12-inch chamber quartz reactor (Fig. 2a) is used in our CVD setup. The setup consists of two graphite electrodes, an infrared detector, and a cooling system. The gases flow through the top shower head to the substrate, and the distance between the top and bottom electrodes is around 10 cm. Compared to the standard tubular CVD systems, our system offers more precise control of the temperature and extremely high cooling rates. Fig. 2b shows a typical sequence of the synthesis steps carried out in this work. First, a piece of Cu foil was placed on the bottom heater and then heated up with flow of H₂ and Ar, which is followed by an annealing step to enable large Cu grains. After annealing, a gas mixture of CH₄, Ar and H₂ is introduced into the chamber. Finally, the sample is rapidly cooled from growth temperature down to around 400 °C in few minutes while flowing high purity Ar gas. The sample is unloaded when the temperature reaches below 100 °C.

### 3. Mechanism of graphene growth on Cu using LPCVD

CVD growth of graphene on Cu is generally attributed to the low solubility of carbon (<0.001 at.%) in Cu and the surface diffusion of carbon atoms on Cu. Nevertheless, it is crucial to understand the details of the nucleation and growth kinetics in order to improve the uniformity and quality of graphene. Graphene growth is a catalytic process, involving hydrocarbon decomposition and surface diffusion, which involves: (1) absorption and de-absorption of hydrocarbon molecules on Cu, (2) decomposition of hydrocarbon to form carbon atoms, (3) aggregation of carbon atoms to nucleation centers, (4) diffusion and attachment of carbon atoms to nucleation centers to form graphene film (Fig. 3a-bottom). Due to strong C–H bonds in methane molecule (440 kJ/mole), its thermal (non-catalytic) decomposition occurs at very high temperatures (>1200 °C) [18]. Different transition metal catalysts (e.g., Fe, Co, Ni, Cu) have been used to reduce the minimum temperature of methane's thermal decomposition. However, Fe, Co, and Ni are not preferred for mono or bilayer graphene growth due to their higher-than-desirable capability to decompose hydrocarbons. On the other hand, the lower decomposition rate of methane on Cu (since Cu can not form carbide with carbon thereby resulting in low solubility of carbon in Cu) allows the possibility of controlling the number of graphene layers.

At a constant temperature, the methane decomposition rate on an ideal flat Cu surface should be uniform. However, the Cu film used for graphene growth is not single crystal, there are many atomic steps, and grain boundaries on the Cu surface even after annealing. These sites usually have much higher chemical activation energy than those of the flat regions of Cu. Therefore, hydrocarbons prefer to decompose on the sites with high activation energies (such as grain boundaries and surface steps) to form nucleation centers. The above deductions have also been confirmed by our experiments.
experimental observation. Fig. 3b shows the SEM image of graphene domains on Cu surface. Graphene domains prefer to grow along the direction of the polish lines (polish lines are created on the Cu surface during the polishing process by the manufacturer) on the Cu foil, which is shown along the white arrow in Fig. 3b. Fig. 3c shows the SEM image of a single graphene domain, which has a tetragonal shape. At the center of the graphene domain, there is a black spot, which is the nucleation site of graphene. The lobe structure domain (in monolayer graphene) [14] and hexagonal domains (in few layer graphene) [19] have been reported. To the best of our knowledge, this is the first observation of the tetragonal shape graphene domains. The existence of different graphene domain shapes indicates that graphene growth is strongly affected by growth conditions.

Fig. 3d shows the optical microscope image of a CVD grown graphene sheet verifying the growth mechanism outlined in Fig. 3a. There are three different visibly contrasting regions in the optical micrograph image. The region with purple color and blue circle is the original nucleation center of graphene, which has a multilayer or few layer structure according to its contrast and the Raman spectra in Fig. 3e (blue line). The Raman spectra of graphene (Fig. 3e) corresponding to the different colored regions shown in Fig. 3d, also indicates that away from the nucleation sites, few or 1–2 layer graphene (red and green circles in (d)) is formed as well as the quality (reduced D peak) and uniformity of graphene improves. From Fig. 3b–e, we conclude that multilayer and few layer graphene starts to grow from the nucleation centers and merge into a 1–2 layer graphene film away from the nucleation centers. The above discussion points to the fact that it is crucial to reduce the number of imperfections and make the surface as uniform as possible to obtain high-uniformity graphene on Cu. The graphene growth rate and number of layers are determined by the diffusion rate of carbon atoms, which in turn, is influenced by the temperature and concentration of the available carbon atoms on the Cu surface. High diffusion rate and high carbon concentration results in multi-layer or few layer graphene. Therefore, to control the number of graphene layers and growth rate, the concentration of the carbon atoms on the Cu surface should be well controlled. Since the concentration of the carbon atoms depends on the partial pressure of the hydrocarbon gas at a given temperature, controlling the partial pressure is also a critical factor for the high-quality growth of graphene. Based on the above understanding of the graphene growth process, we investigated the role of graphene growth parameters through a LPCVD process on Cu.

4. High-uniformity graphene growth and optimization

4.1. Importance of substrate pretreatment

As discussed in Section 3, the surface treatment of the Cu foil is a critical parameter that affects the growth of high-quality graphene. Before growth, thorough cleaning of Cu surface is necessary to avoid effect of uncertain materials on graphene growth. Dilute acid is usually used to remove the native Cu oxide, but it makes the Cu foil surface rough after the anneal-
ing, which results in poor quality graphene. In our experiments, we found that employing ultrasonic to clean the Cu foil in acetone for 10 min is very helpful for improving the quality of graphene.

Fig. 4a shows the OM image of Cu foil surface after being annealed at 990 °C, 80 mbar, and 10 sccm H2/150 sccm Ar for 20 min. AFM is employed to study the surface roughness of Cu. AFM image (Fig. 4b) of Cu surface annealed at 80 mbar shows several steps on the surface. The height distribution of these steps is also measured along the red line in Fig. 4b. The highly dense and sharp structures, which are shown in Fig. 4c, lead to higher decomposition rate of methane during graphene growth. We have also investigated the effects of decreasing the annealing pressure (from 80 to 20 mbar) on the quality and uniformity of graphene. It was observed that the surface of Cu becomes smoother due to the increasing sublimation of Cu at lower pressure. As shown in Fig. 4d–f, low pressure annealing could greatly enhance the uniformity of Cu surface and decrease the number of the sharp structures, thereby making the Cu surface smoother.

The uniformity and quality of the graphene grown under different annealing conditions (80 mbar and 20 mbar) is also investigated by transferring graphene onto the SiO2 (300 nm)/Si substrate. Fig. 4g shows the corresponding OM image of the graphene transferred from the Cu foil in Fig. 4a and it is very clear that there are many blue lines, which are the multilayered graphene in the film. This proves our proposed mechanism that the grain boundaries and the imperfections (the sharp structures shown in Fig. 4c) have much higher ability to decompose methane. Although the graphene film consists of many multilayer regions, the area between these multilayer regions is confirmed to be monolayer or bilayer graphene through the Raman spectra (Fig. 4h) with obvious defects. This phenomenon implies that the graphene film tends to have lower number of layers away from the nucleation centers. Hence, to obtain high uniformity graphene on Cu, it is crucial to reduce the amount of imperfection sites and to make the surface atomically flat by proper annealing.

When the annealing pressure of the Cu substrate decreased from 80 to 20 mbar, the Cu surface becomes much smoother. The corresponding graphene film (Fig. 4i) transferred from flatter Cu sample (Fig. 4d) shows better uniformity compared with that of the sample (Fig. 4a) annealed at 80 mbar. It can be observed that there is no obvious multilayer graphene (blue) region in Fig. 4i. Fig. 4j shows the Raman spectra of the synthesized graphene (in Fig. 4i) indicating high-quality without any obvious defects.

4.2. Effects of hydrocarbon concentration

It is well known that the catalytic properties of metal catalysts strongly depend on their surface orientation [20]. After low pressure annealing, the Cu surface becomes smoother and has low-index planes (such as (1 0 0) plane) due to the restructuring of the Cu atoms enabled by increased diffusivity at high temperatures during the low pressure annealing. Thus, most of the Cu surface attains similar surface orientation and thereby similar ability to decompose hydrocarbons. Under such conditions, the importance of the partial pressure of the hydrocarbon gas increases since it becomes the main factor determining the graphene growth, which in turn, is
determined by the concentration of carbon atoms on the Cu surface. Higher growth temperature is better for graphene growth on Cu because the Cu is not a good catalyst for decomposing methane. Fig. 5a and b shows growth of graphene domains at different temperatures. When the growth temperature is 880°C, size of the graphene domains is smaller than when the growth temperature is 980°C. In our experiments, we found that there is a minimum partial pressure (of hydrocarbon) requirement for graphene to cover the Cu surface completely. When the growth temperature is 980°C, the minimum flow rate of methane is 8 sccm at a total pressure of 1 mbar. As shown in Fig. 5f, the Cu surface is covered by wrinkled graphene film. Usually, the graphene forms wrinkles on the Cu surface no matter what the graphene domain size is (Fig. 3c shows that the 1 μm size graphene domain also has wrinkles). However, when the partial pressure of methane is lower than this minimum value, Cu surface is only covered by separate graphene domains (Fig. 5a–e). Moreover, the density and size of these graphene domains have narrow variation ranges under the growth conditions shown in Fig. 5b–e. Although the growth parameters marked in Fig. 5b is similar to the parameters reported by Li et al. [21], graphene growth shows a different growth behavior, such as the different domain size and domain shapes. This difference indicates that the graphene growth might be greatly influenced by some other factors, such as surface treatment.

As shown in Fig. 5g–i, low partial pressure of hydrocarbon could greatly decrease the size of nucleation centers and thereby enhance the uniformity of graphene. When the flow rate of methane is 40 sccm, high-density blue dots (representing multilayered regions) appear on graphene resulting in low uniformity. On the other hand, when the flow rate of methane is decreased to 20 sccm, the size of the blue dots also decreased. With further reduction of the flow rate of methane to 13 sccm, only a few blue dots can be observed within a one hundred micrometer scale. From Fig. 5g–i, it can be concluded that decreasing the partial pressure of methane decreases the probability of adsorption of methane on Cu surface, and thereby decreases the number of carbon atoms decomposing on the Cu surface, resulting in smaller nucleation centers and lower growth rate, and subsequently improves the uniformity of graphene. We also noticed (Fig. 5a–f) that further reduction of the methane flow rate (below 13 sccm) would still result in formation of bilayer graphene on the low (99.8%) purity Cu foils at 980°C, while the growth of monolayer graphene is difficult. This motivated us to study the effects of substrate purity of Cu on the number of graphene layers along with their uniformity and quality, as detailed in the following sub-section.

4.3. Effect of purity of the Cu substrate

In all of the above experiments, we found that using Cu foils with the purity of 99.8% resulted in the growth of bilayer graphene under different growth conditions used in this work. It is well known that the impurity in the catalyst greatly enhances the catalytic capability of the catalyst. Since there is about 0.2% unknown-impurity in our Cu foil, could the purity of the Cu foil affect the number of layers? To investigate this, we used Cu foils with both high purity (99.99%) and with
purity of 99.8% in the CVD chamber at the same time and under the same annealing and growth conditions. Using Raman spectra to evaluate the monolayer and bilayer CVD (non-AB stack) graphene is difficult because their Raman spectrum is variable due to the different doping level of CVD graphene after high temperature process [5,10,14,22]: the ratio of $I_{2D}/I_G$, peak positions of G and 2D peaks is related to the doping level of graphene. However, our two graphene samples are grown under same conditions, which can minimize the effect of doping. Comparison of the Raman spectra (Fig. 6a) and the statistics of the 2D peak positions vs. ratio of $I_{2D}/I_G$ (Fig. 6b) of both samples, reveals obvious differences. Raman spectra (blue line) of the sample grown on the low purity (99.8%) Cu foil has a 2D peak position with a range of 2641–2646 cm$^{-1}$ and the $I_{2D}/I_G$ varying from 1.8–2.4, indicating bilayer graphene. However, $I_{2D}/I_G$ of the Raman spectra (red line in Fig. 6a) taken from the graphene grown on high purity Cu (99.999%) is above 3 and has 2D peak position in the range of 2638–2641 cm$^{-1}$, indicating monolayer graphene. Nevertheless, optical contrast can also assist in evaluating monolayer and bilayer CVD graphene [22]. OM image of the CVD graphene grown on the low purity and high purity Cu foil transferred by thermal release tape are taken at the same illumination intensity and magnification. As shown in Fig. 6c, the sample grown on high purity Cu exhibits lighter contrast than the graphene grown on low purity Cu (as shown in Fig. 6d). Additionally, the electron diffraction pattern taken from the sample (in Fig. 6d), as discussed in Section 5, confirms that the number of CVD graphene layers with non-AB stacking as determined through the combined analysis of Raman spectroscopy and optical contrasting is reliable.

Recent studies on the graphene growth optimization indicate that hydrocarbon pressure is one of the major factors affecting the graphene growth [12,19]. The pressure of the hydrocarbon determines the concentration of the carbon atoms on the Cu surface during graphene growth. It is believed that the impurity atoms in the Cu diffuse to the Cu surface during annealing. These surface impurities dramatically enhance the catalytic capability of Cu resulting in high concentration of carbon atoms that are decomposed from methane. Bilayer graphene growth requires double the amount of carbon atoms than the case of monolayer graphene, which implies that bilayer graphene growth involves higher concentration of carbon atoms (since synthesis of both bilayer and monolayer graphene is achieved simultaneously guarantying identical conditions). Hence, it can be concluded that the purity of Cu surface plays a critical role in determining the number of graphene layers.

### 4.4. Optimization of graphene transfer process

To transfer large-scale continuous graphene, a common technique is to use a thin layer of poly methyl methacrylate (PMMA) as the protection layer due to its flexibility. PMMA/graphene films float in the etchant after the Cu substrate is wet etched by iron nitrate. PMMA/graphene films were then manually transferred to the desired substrate. Finally, PMMA is removed by stripper (such as acetone). Since it is difficult to
remove the PMMA completely, an additional annealing step (at \(450^\circ C\)) is required to remove the residual PMMA on graphene [12]. However, annealing can introduce defects in graphene (as discussed in the next paragraph). To avoid annealing, we applied methyl methacrylate (MMA)/PMMA as the protection layer, in which MMA was directly spin-coated on the graphene as a buffer layer between graphene and PMMA. MMA is a smaller molecule and is therefore much easier to remove by standard lift-off techniques as compared to PMMA.

To estimate the effect of annealing on the quality of graphene, a back-gated bilayer graphene field effect transistor (FET) was fabricated on the \(\text{Al}_2\text{O}_3\) (72 nm) substrate (Fig. 7a), which was deposited on highly doped n-type Si (\(<0.004 \text{ \Omega cm}\)) wafers by plasma-assisted ALD at 300 °C. After transferring the graphene on the substrate and removing the MMA/PMMA protection layers, we fabricated the FET devices in one uniform piece of graphene using SnO\(_2\) microribbon as a shadow mask. The contact patterns were then defined by e-beam lithography followed by 5 nm Ti and 150 nm Au depositions by e-beam evaporator to form the electrodes. Fig. 7b shows the OM image of the fabricated back gated FET device on \(\text{Al}_2\text{O}_3\) (72 nm)/Si substrate. The transfer characteristics curve (Fig. 7c, black curve) of CVD graphene exhibits obvious ambipolar behavior and the neutral (Dirac) point is at 0.5 V. Note that at the Dirac point, the electron and hole density in the system are the same. The device was subsequently annealed at 50 mbar, \(450^\circ C\), and 500 sccm Ar/10 sccm \(H_2\) for 5 min, which is common condition for removing the residual PMMA on graphene. The red curve in Fig. 7c shows the transfer characteristic after annealing and it can be observed that the neutral point shifts to around 10 V, which indicates that the graphene has become p-doped after annealing. The carrier mobility \(\mu\) can be calculated from \[\mu = \frac{L(W/C_0)V_{ds}}{\Delta I_{ds}/\Delta V_{gs}}\] to further estimate the quality of graphene. \(C_0\) is the gate capacitance per unit area; \(L\) and \(W\) are the channel length and width, respectively; \(V_{gs}\) is the intrinsic drain voltage excluding the contact resistance. The carrier density of bilayer graphene FET (Fig. 7d) can be extracted by the method proposed by Fang et al. [23]. From the transfer characteristics curve of graphene FETs on \(\text{Al}_2\text{O}_3\) shown in Fig. 7c (before annealing, black curve), the hole and electron mobilities were extracted to be 3600 and 2860 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) at \(V_{gs} = -3.2\) V and \(V_{gs} = 3\) V, respectively. Note that due to process variations, the devices have different carrier mobilities under identical process conditions. The performance shown in Fig. 7c is from one of the devices, while for the best device under the same process conditions, a maximum hole (electron) mobility of 5500 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) (3900 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\)) was achieved. By comparing the values of \(\Delta I_{ds}/\Delta V_{gs}\) (from Fig. 7c, black and red curves), it can be estimated that the hole mobility decreases by 39.5% after annealing. This result indicates that hydrogen annealing can introduce defects in graphene and can thereby degrade the device performance of graphene even at relatively low temperatures. Usually, SiO\(_2\)/Si substrate is used for graphene device fabrication due to the fact that the SiO\(_2\) with certain thickness on silicon supplies visual contrast to observe graphene. For comparison, FET device based on CVD graphene is also fabricated on SiO\(_2\) (300 nm)/Si substrate. However, transfer characteristics curve (Fig. 7e) shows that graphene is

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1 The corresponding hole and electron densities are \(2 \times 10^{12}\) and \(1.2 \times 10^{15}\) \(\text{cm}^{-2}\), respectively.
Uniform monolayer or bilayer graphene with dimensions of the substrate. A detailed study about the Al₂O₃ substrate treatment fabricated on Al₂O₃ substrate could be attributed to two possible reasons: (1) thin dielectric film allows strong electric field. (2) less substrate doping due to the different chemical bonds on the Al₂O₃ surface compared with that of SiO₂ substrate. The excellent device performance of the device fabricated on Al₂O₃ substrate could be attributed to two possible reasons, (1) thin dielectric film allows strong electric field. (2) less substrate doping due to the different chemical bonds on the Al₂O₃ surface compared with that of SiO₂ substrate. A detailed study about the Al₂O₃ substrate treatment will be reported in future work.

5. Atomic structure of CVD graphene

Uniform monolayer or bilayer graphene with dimensions approximately a few hundred microns can be grown on the Cu foil by tuning the annealing and growth condition parameters. Although some of our FET devices exhibit mobilities up to 5500 cm²/V s, this value is still smaller than that of exfoliated graphene (Fig. 1) [24]. Besides the defects introduced in graphene during the above mentioned fabrication steps, the native defects in the atomic structure of CVD graphene should also be investigated due to the nucleation and growth mechanism of CVD graphene discussed in Section 3. Hence, a detailed study of the atomic structure of CVD graphene represents an important step toward understanding the properties of this material. Here, we employed HRTEM to study the atomic structure of CVD bilayer graphene. Fig. 8a shows the TEM image of the graphene on the Cu grid. The electron diffraction pattern (Fig. 8b) that is taken within the purple ring in Fig. 8a shows two sets of hexagonal diffraction spots rotated by approximately 5°, which indicates that the bilayer graphene is non-AB stacked.⁴ High-resolution imaging of graphene shown in Fig. 8c provides insight into the atomic structure of the CVD graphene layers. It is apparent that our CVD graphene is comprised of well crystallized carbon atoms and there is no obvious topological defect in the graphene. Note that due to the limitation of TEM (FEI Tecnai G2) the hexagonal lattice cannot be observed. However, the red lines in Fig. 8c indicate that the 2D lattice structure of CVD graphene consists of several orientations, which not only confirms our proposed growth mechanism in Section 3 but also indicates that the crystal structure of the CVD graphene contains different orientations even within an apparently uniform region as observed in Fig. 8a under low magnification TEM. Furthermore, the area within the green circle (in Fig. 8c) exhibits an obvious gap between two adjacent graphene layers, which points to the existence of another structural defect in CVD graphene. All of these above information indicate that the crystal structure of CVD graphene is not as perfect as that of exfoliated graphene, which results in lower carrier mobility of the CVD graphene.

6. Conclusions

In summary, this paper presented a systematic study of the mechanisms determining the nucleation and growth of high-quality monolayer and bilayer graphene on Cu using LPCVD. A new growth mode of graphene domains was revealed under the low pressure growth conditions. It was found that while substrate annealing (that determines the micro-topography of Cu surface) and partial pressure of hydrocarbon are important factors determining the uniformity of CVD graphene, it is the purity of the Cu film that is crucial for the controlled synthesis of monolayer or bilayer graphene films. The minimum partial pressure of hydrocarbon is also a key factor, which determines the coverage of graphene on Cu surface. Based on the understanding of the above factors, uniform graphene with large domain size (120–210 μm) as well as bilayer graphene with high mobility (up to 5500 cm²/V s) could be produced in a simple and controlled manner. The controllable synthesis of bilayer graphene, such as transferring, annealing and patterning, besides the defects introduced in graphene during the above mentioned fabrication steps, the native defects in the atomic structure of CVD graphene should also be investigated due to the nucleation and growth mechanism of CVD graphene discussed in Section 3. Hence, a detailed study of the atomic structure of CVD graphene represents an important step toward understanding the properties of this material. Here, we employed HRTEM to study the atomic structure of CVD bilayer graphene. Fig. 8a shows the TEM image of the graphene on the Cu grid. The electron diffraction pattern (Fig. 8b) that is taken within the purple ring in Fig. 8a shows two sets of hexagonal diffraction spots rotated by approximately 5°, which indicates that the bilayer graphene is non-AB stacked. High-resolution imaging of graphene shown in Fig. 8c provides insight into the atomic structure of the CVD graphene layers. It is apparent that our CVD graphene is comprised of well crystallized carbon atoms and there is no obvious topological defect in the graphene. Note that due to the limitation of TEM (FEI Tecnai G2) the hexagonal lattice cannot be observed. However, the red lines in Fig. 8c indicate that the 2D lattice structure of CVD graphene consists of several orientations, which not only confirms our proposed growth mechanism in Section 3 but also indicates that the crystal structure of the CVD graphene contains different orientations even within an apparently uniform region as observed in Fig. 8a under low magnification TEM. Furthermore, the area within the green circle (in Fig. 8c) exhibits an obvious gap between two adjacent graphene layers, which points to the existence of another structural defect in CVD graphene. All of these above information indicate that the crystal structure of CVD graphene is not as perfect as that of exfoliated graphene, which results in lower carrier mobility of the CVD graphene.

Fig. 8 – (a) TEM image of CVD bilayer graphene (area containing the purple ring) on Cu grid. (b) Electron diffraction patterns taken within the purple ring in (a). (c) High resolution transmission electron microscopy (HRTEM) image of bilayer graphene. Red lines are along the direction of the carbon lattice atoms, which also indicates the existence of different orientations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

⁴ The corresponding hole and electron densities are 1.7 × 10¹² and 0.8 × 10¹² cm⁻², respectively.
⁵ AB stacked bilayer graphene is usually obtained from exfoliated graphite and diffraction spots arising from each of the two layers are not distinguishable.
graphene achieved in this work for the first time could be valuable for designing bandgap engineered electronic devices. Finally, HRTEM analysis of the atomic structure of CVD bilayer graphene revealed its non-uniform nature arising due to different lattice orientations and structural defects. This observation provides useful insights for understanding the growth mechanism of CVD graphene and for optimization of the growth process to further improve the quality of CVD graphene.

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