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1   **Controlled Removal of Monolayers for Bilayer Graphene**

2   **Preparation and Visualization**

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12   **Abstract** Bilayer graphene, unlike monolayer graphene, provides a

13   tunable electronic energy gap when an electrical field is applied across

14   the layers, therefore holds great potential in semiconductor industry. Here,

15   we demonstrate a facile technique to obtain bilayer graphene structures

16   on the growth substrate by controlling oxidation to remove monolayers,

17   while retaining the bilayer electronic properties. We found that this

18   precise oxidation process selectively destructs monolayers while

19   preserves the qualities of bilayers, evidenced by the expected quantum

20   hall effect and exceptional room temperature carrier mobilities of ~3500

21    $cm^2v^{-1}s^{-1}$ obtained from electrical transport measurement. In addition,

22   visualization of bilayers, which serves as nuclei for graphene growth,

23   opens the door for the understanding the actual mechanism of graphene

24   growth process which eventually can lead to the optimized synthesis.

25

Introduction

Graphene is a promising material for electronic applications, but their intrinsic gapless semimetal nature hurdles their applications in semiconducting industry. On the other hand, bilayer graphene, in particular for AB Bernal stacking order, can provide a tunable bandgap when an electrical filed is applied across the layers, hence forth attracted considerable attention for its potential application in logic circuit[1-3]. To obtain large size graphene thin films for practical applications, Chemical Vapor Deposition (CVD) method[4-6] was developed to synthesize monolayer graphene thin films, which was later extended for bilayers or few layers graphene preparation. However, current processes always produce graphene films that contain a significant portion of monolayer, which will have detrimental effects when used in semiconductor devices. Moreover, it would be also desirable to directly observe the structure and overall distribution of graphene nuclei during CVD growth, in order to understanding the underlying kinetics for graphene growth. Previously, a simple optical method has been developed to directly visualize monolayer graphene grains on Cu foil, taking advantage of their different contrast between graphene-covered and uncovered region after mild oxidation[7]. However, visualizing bilayer graphene has not been reported so far, due to the difficulties of gaining contrast between bilayer and monolayer graphene. Consequently, characterization methods for bilayers on Cu substrate are mainly limited to localized methods such as scanning electron microscopy (SEM)[8] and atomic force microscopy (AFM)[9], which precludes us from obtaining a full map of graphene distribution on copper substrate, or limiting us to an

1   optical method by transferring the post-synthesized graphene onto silicon wafer of

2   300 nm SiO_2[10].

3   Here we show a simple method that enables us to solve the purification and direct

4   visualization issue at the same time. This is achieved by controlling the oxidization of

5   the post-growth monolayer and bilayer graphene/Cu substrate in air at a raised

6   temperature, utilizing their different resistance to oxidation. Controlled oxidation

7   renders the Cu metal covered by monolayer easily oxidized, while area covered by the

8   bilayers are only insignificantly affected, and consequently leads to the contrast for

9   the monolayer and bilayer covered region. Electron transport measurement on

10   bilayer-based FET devices confirms that the quality of bilayers are well preserved

11   during this controlled oxidation process.

12

13   **Results and Discussions**

14   We firstly demonstrate a controlled oxidation method by showing the evolution of

15   graphene grains during this process. **Figure 1** illustrates a sequence of optical images

16   recorded at end of annealing at 200°C for 30s, followed by annealing in air at 300°C

17   for additional 30s, 60s, 90s and 120s, respectively. At the early stage of annealing, the

18   contrast of monolayer to copper substrate gradually increases and reached a maximum

19   after annealing at 300°C for ~60s concurrent with the observation that copper

20   substrate turning from red to light green in this process (for more images, see fig. S1

21   of Supplementary Information). Additional annealing at 300°C for 90s induces a

22   sudden decrease in contrast between monolayers and copper substrate, while

3

1   simultaneously reveals the bilayer nucleus in the center of the graphene grain. After

2   additional annealing at $300^{\circ}C$ for 120s, majority of the monolayers are broken into

3   fragments and the nucleus stand out sharply. In addition, we note that a significant

4   number of cracks emerge along the edges of nucleus, as shown in figure 1f, implying

5   that the oxidation for nucleus may start from the edges. Similar result can be obtained

6   if lower annealing temperature but longer duration is used, for example, after

7   exposing the graphene/Cu sample in air for several months (fig. S2 of Supplementary

8   information), the nuclei also become visible.

9   **Figure 2** illustrates the detailed surface morphology acquired by atomic force

10   microscope (AFM). The after-oxidation morphology of regions that were previously

11   covered by monolayer, *i.e.* in the outer part of the graphene (fig. 2b and corresponding

12   profile in 2d) shows that monolayer grain has been broken into fragments, possibly

13   are damaged by the copper oxide particles or stripes formed after the oxidation,

14   whereas the bilayer nucleus are intact with only a few insignificant damages (fig. 2c

15   and corresponding profile in 2d), consistent with the result shown in figs 1f. The

16   formation of oxide particles or stripes after oxidation has been elaborately studied by

17   many groups[5, 11-12](also see XPS results in Figure S6 of supplementary information)

18   and the size ranges from nanometer to micrometer scales, depending on degree of

19   oxidation and temperature. As a result of nanoparticle's volume expansion, stress will

20   be induced on the monolayer graphene, which also leads to their reactivity

21   enhancement. Following the oxidation on those sites, defects and cracks will expand

22   to larger cracks, which allows more exposure to oxygen for the Cu substrates. As

1   shown in figure 2a, a crack are also occasionally seen on some bilayers regions, but

2   typically has limited effect on electronic quality as will be shown in latter part of the

3   discussion.

4   The method reported here provides insights on possible oxygen diffusion path

5   during the oxidation. Previously study has shown that graphene is impermeable for

6   most gas, including helium[13]. Therefore, the most likely paths for oxygen to attack the

7   graphene-covered region are 1) from above through defects or atom exchange

8   mechanism[14], or 2) from bottom through the micro-space/ripples formed between

9   grains and copper substrate. One would expect the former path is more common, as

10   defective sites usually has high reactivity, as it was observed that the methane

11   decomposition usually started at those defective sites which includes impurities[15],

12   metal step[16] or metal particles[5]. This diffusion path, however, does not agree with our

13   experimental observation that only insignificant damage were observed at the nucleus

14   center, while the majority of cracks are near the edges. Instead, our observation

15   supports that oxygen may attack the monolayers from underneath. Indeed, micrometer

16   scale periodical ripples[5, 8] are widely seen for CVD-grown graphene due to the

17   thermal expansion coefficient mismatch between graphene and copper substrate

18   during cooling process. Those ripples form easy accessible channel for oxygen

19   diffusion (Fig. S3 of Supplementary Information). Nevertheless, the oxygen path may

20   also dependent on the temperature, as crack and pits are also seen in the graphene

21   terrace when the sample is placed in air at room temperature for an extended period

22   (Fig. S2 of Supplementary information). In addition, electrochemical erosion may

1   have also involved in this process[17].

2   **Figure 3** depicts further characterization of the visualized bilayer/few layers

3   graphene structure. Figure 3a illustrates the scanning electron microscopy (SEM)

4   image of a typical bilayer/few layers graphene flake synthesized by CVD[5], which

5   were embedded at the center of a large single crystal graphene monolayer (inset of Fig.

6   3a). The monolayer graphene shows asymmetric structure of diameter ~1mm,

7   consistent with our previous report. After annealing the sample in air under 300 ℃

8   for 2 minutes, intense contrast were obtained for the bilayer nucleus at the center,

9   where the monolayer-covered region become less reflective and turned to dark color,

10   as shown in Fig. 3b (see more images at Fig. S4 in the supplementary information

11   section). As will be clarified later from Raman measurement, this originated from the

12   destruction of the monolayer, concurrent with copper substrate oxidation. By using

13   this method, the nucleus region stands out sharply against original graphene flake

14   region, due to the contrast resulted from reduced reflectance. Interestingly from this

15   visualization method, we observed some individual hexagonal shape grains have more

16   than one nucleus in the center (Supplementary Fig.S2), contrary to common belief

17   that each graphene flake was grown from a single nucleus. More work is in progress

18   to understand this phenomenon.

19   To understand the nature of graphene nucleus, we performed the Raman

20   characterization on the sample after it was transferred onto 300 nm oxides thickness

21   silicon wafer. As shown in **Figure 3c**, the outer region of the original graphene flakes

22   show mostly broken graphene fragments. Single point Raman spectrum at site 1,

6

1   shown in figure 3d, displays an enhanced D peak (~1350 cm^{-1}) for monolayer

2   graphene, with typical monolayer G and 2D bands appears at 1580 and 2680 cm^{-1},

3   respectively. In contrast, Raman spectrum at sites 2 and 3 reveals bilayer

4   characteristics, but with distinct 2D and G band intensity ratio (I_{2D}/I_G) of ~2.89 and

5   0.51, respectively. These Raman features indicate that the bilayer graphene grains at

6   sites 2 and 3 corresponds to AB Bernal stacking and non-AB twisted stacking

7   respectively[18-19].   We have also performed Raman mapping to get a full map of the

8   nucleus structure, shown in figs.3e-g. Accordingly, the 2D peak intensity map shows

9   only two main areas, corresponding to the Bernal stacking and non-AB twisted

10   turbo-stacking modes, demonstrating high uniformity in those respective areas. It

11   appears that the D band intensity is also weakly dependent on the stacking order[20], as

12   we can clearly observe the outline of those two regions in the D band map in fig. 3g.

13   Those results confirm that our controlled oxidation process breaks monolayer

14   graphene but has introduced only insignificant amount of defects on the bilayer

15   nucleus.

16

17   Previous reports show that monolayer graphene are stable in air at temperature up

18   to 400 ℃ on silicon substrate[21]. The fact that we can "remove" the monolayers, *i.e.* to

19   break continuous monolayer into discontinued fragments that disrupt their structure

20   continuity, at only 300°C suggests that it is possible to lower oxidation resistance of

21   monolayers at appropriate conditions. The key feature in our method is that we

22   utilized the intrinsic reactivity difference between various numbers of layers, which is

1   further amplified by their curvatures induced by their supporting metal surface, which

2   is larger for monolayers than multi-layer structures[22]. Reactivity of carbon nanotube

3   or fullerene, compare with flat graphene structures, was shown to enhance remarkably

4   because of curvature[23-24]. Other contributing factors may include enhancement from

5   the underneath copper substrate and/or defects in CVD graphene[25]. More recent work

6   has shown that the reactivity of graphene can be greatly enhanced by the substrate.[26]

7   Other morphological features such as the graphene wrinkles, which enhances the

8   reactivity due to curvature effect, can also play very important roles under oxidation

9   environment[27]. It would be difficult to completely remove all the resulted monolayer

10 fragments, however, the small sizes of those fragments, normally within hundreds of

11 nanometers, will disrupt the structure continuity and thus disrupt electrical/thermal

12 connectivity, in contrast to the only insignificantly damaged bilayers.

13   Electric transport measurement was conducted to investigate the electronic

14 properties of the bilayer graphene structures obtained with this approach. We used

15 Electron Beam Lithography (EBL) to fabricate bilayer graphene field effect transistor

16 (FET) in a hall bar geometry shown in **Figure 4a**, after the post-oxidation bilayer

17 graphene was transferred onto 300nm oxide silicon wafer. Before electrodes (10 nm

18 Ti and 40 nm Au) were deposited, the graphene sample was annealed in vacuum

19 system to improve the contact between graphene and substrate. Figure 4 illustrates the

20 sheet resistance as a function of gate voltages measured under a vacuum of 10 Torr at

21 temperature 2K, 100K, 200K and 300K. All four curves show typical ambipolar

22 behavior of graphene FET devices, confirming the high quality of bilayer graphene

1   prepared with this method. The mobility is determined to be $\mu_e = 3520$

2   ($\mu_h = 3490$)and $\mu_e = 3750$ ($\mu_h = 3590$)cm^2·v^{-1}·s^{-1}respectively at 300K and 2 K,

3   significantly higher than the reported RT value of ~500 cm^2·v^{-1}·s^{-1}for LPCVD[3, 28], and

4   recent bilayer graphene in the range of 1400-4400[29], compared to defect-free

5   mechanically exfoliated bilayer graphene[30]. Here the carrier mobility was obtained by

6   the equation $\mu = \left(1/C_g\right)\partial\sigma/\partial V_g$, where $\sigma = 1/\rho_{xx}$ is the sheet conductance and

7     $C_g = 1.15 \times 10^{-8}$ F/cm^2 is the back gate capacitance. Moreover, we investigated the

8   Quantum Hall effect (QHE) on the device to study the quality of the bilayer graphene.

9   Figure 5b plots the longitudinal resistance (R_{xx}) and Hall resistance (R_{xy}) as a function

10   of the back gate voltage which was measured at 2 K with a perpendicular magnetic

11   field B = 9 T. Pronounced plateaus can be clearly seen in the Hall resistance $R_{xy} =$

12     $\pm h/4Ne^2$ with $N \geq 1$, which are accompanied by the oscillations in the longitudinal

13   resistance R_{xx}. The well-shaped and symmetric QHE indicates a high quality of our

14   CVD bilayer graphene, comparable to the mechanically exfoliated bilayer graphene[31].

15

Conclusions

17   In summary, here we developed a simple method to directly visualize bilayer

18   graphene nucleus on the growth Cu substrate. With this method, we were able to

19   visualize the structure of bilayer nucleus on copper by controlled oxidation in air. The

20   key is that we utilize the lower oxidation resistance for monolayer graphene, which is

21   further enhanced by the induced mechanical strain applied from the underneath

22   oxidized Cu nanoparticles. On the other hand, the structure of bilayer graphene is less

1   affected as confirmed by Raman and electronic transport measurement. The

2   visualization technique reported here gives us a tool to fast observe the nucleation

3   formation process in the chemical vapor deposition, and would enable fundamental

4   study of graphene growth with controlled number of layers by providing statistically

5   important information about graphene growth.

6

7

1 **Methods**

2 **Copper foil pretreatment**   Here we use copper foil purchased from Alfa Aesar

3 (Stock no. 13382) to synthesize graphene grains. Copper foil was cut into small size

4 (around 2cm × 8 cm) and then chemically polished with $FeCl_3$ (5g $FeCl_3$, 10 mL

5 HCl and 100 mL DI water) in ultrasonic for 10-15 seconds. After that, polished

6 copper foil was rinsed with DI water for at least three times to remove residues.

7 Finally, copper foil was blow-dried with nitrogen.

8 **Graphene synthesis by chemical vapor deposition**   Polished copper foil was

9 loaded into 1 inch diameter quartz tube and purge with 350 sccm high-purity argon

10 gas for at least 20 minutes. The system temperature were then ramp to 1050 ℃

11 within 30 minutes, followed by charging with 15 sccm high-purity hydrogen and 15

12 sccm methane (500ppm in Ar) and kept for 1 hour to grow large sized graphene

13 grains.

14 **Graphene transfer**   Graphene is transferred by electrochemical method, similar as

15 previous report[32]. 1 M NaOH is used as electrolyte, while saturated calomel electrode

16 and Pt are used as reference and counter electrodes, respectively.

17 **Characterizations**   SEM was done using a JEOL 6390 scanning electron

18 microscope operated at 20 keV. The Raman spectrum was recorded with a Renishaw

19 Raman RM3000 scope using a 514 nm excitation argon laser. Mapping condition:

20 20×objectives lens, with 1.5 µm step in both X and Y axis. AFM was scanned under

21 semi-contact mode using a NTEGRA probe NanoLaboratory (NT-MDT, Inc.) with

22 ACTA tips from AppNano at 1.5 Hz scan rate and 512×512 resolutions. Optical

1   images were taken by a LEICA DFC 290 optical microscope.

2   **Device fabrication and electronic measurement**   Graphene layers, after being

3   transferred onto the 300 nm oxide Si wafer, was first defined into the Hall Bar

4   geometry by using e-beam lithography (Raith e-LiNE, 10 kV) and then etched by

5   oxygen plasma[33]. Metal contacts were defined by a second e-beam lithography step

6   followed by e-beam evaporation of 10 nm Ti and 40 nm Au. The contact resistance is

7   usually on the order of several hundred Ohms. All the measurements were carried out

8   in Physical Property Measurement System (PPMS, Quantum Design). Before

9   measurement, graphene samples were heated in situ to 380 K in high vacuum for

10   several hours to remove the adsorbed water molecules and PMMA residues. Electrical

11   measurements were carried out by using a Keithley 6221 AC/DC source and a

12   Keithley 2182A nanovoltmeter. Four-probe method was used during measurement to

13   avoid contact resistance.

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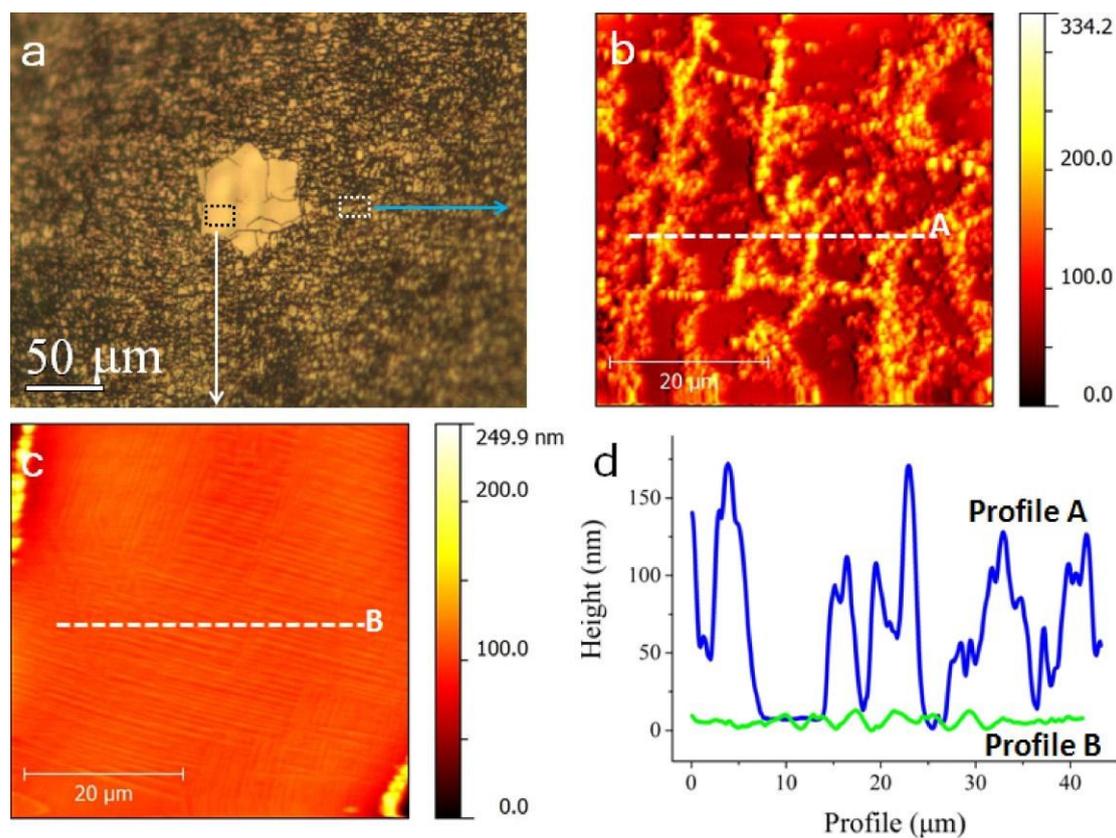J.-J. Lin, P. Sheng, *Phys. Rev. Lett.* 2013, **110**, 066805.
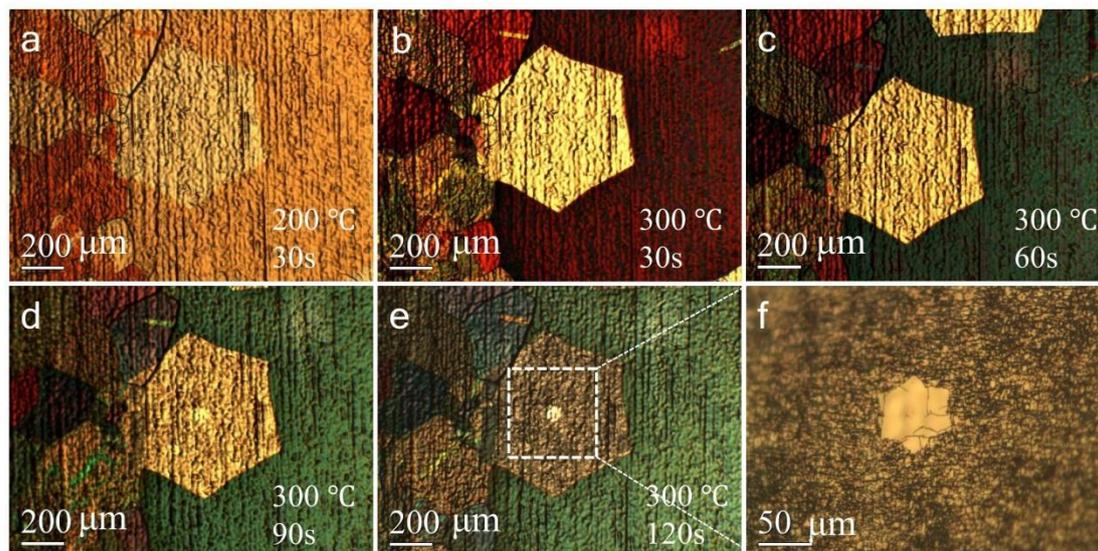
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2 **Figure 1 | Evolution of monolayer/bilayer on copper substrate under controlled**

3 **oxidation.** (a) annealing at 200°C for 30s in air. (b-e) additional annealing at 300°C in

4 air recorded at 30s, 60s, 90s and 120s.   (f) Enlarged image of 3e.

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2 **Figure 2 |Morphology comparison of monolayer and bilayer region after**

3 **oxidation.**   (a) Optical image for post-oxidation bilayer nucleus on copper. (b, c)

4 AFM images for grains of monolayer and bilayer nucleus regions, respectively. (d)

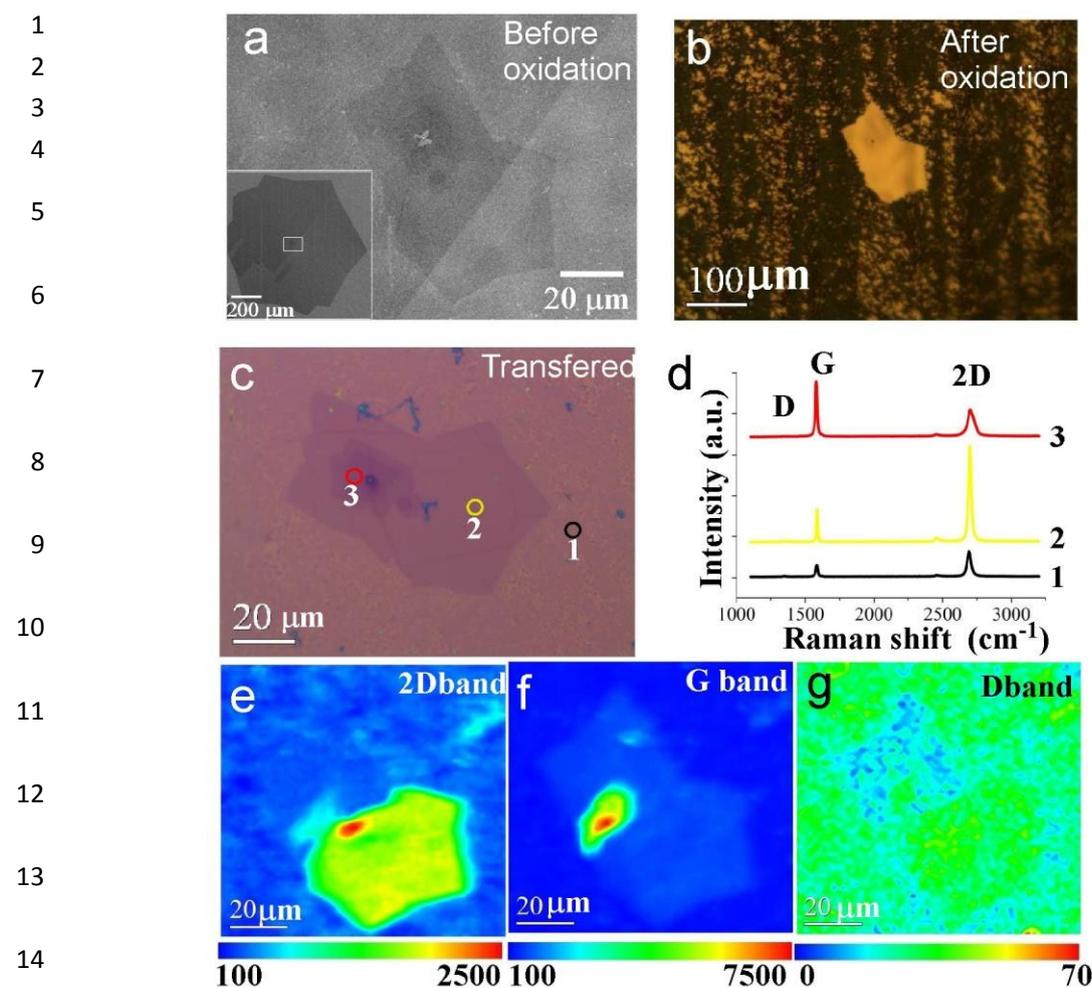5 Height profiles along the lines in 2b and 2c, respectively.

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Figure 3 Bilayer/few layers properties. (a) SEM images of bilayer/few layers graphene grain on copper before oxidation. Inset indicates the overview of the whole flake. (b) Optical images for the same grain on oxidized copper (200 ℃, 30s annealing in air and then additional annealing at 300 ℃ for 120s). (c) Optical image after transferred onto 300nm oxide substrate. (d) Raman spectrum at 3 spots on nucleus. Site 1, 2 and 3 shows monolayer fragments, typical non-AB stacking and AB stacking bilayer characteristics, respectively. (c-e) Raman mapping of 2D, G and D band for the bilayer/few layers region.
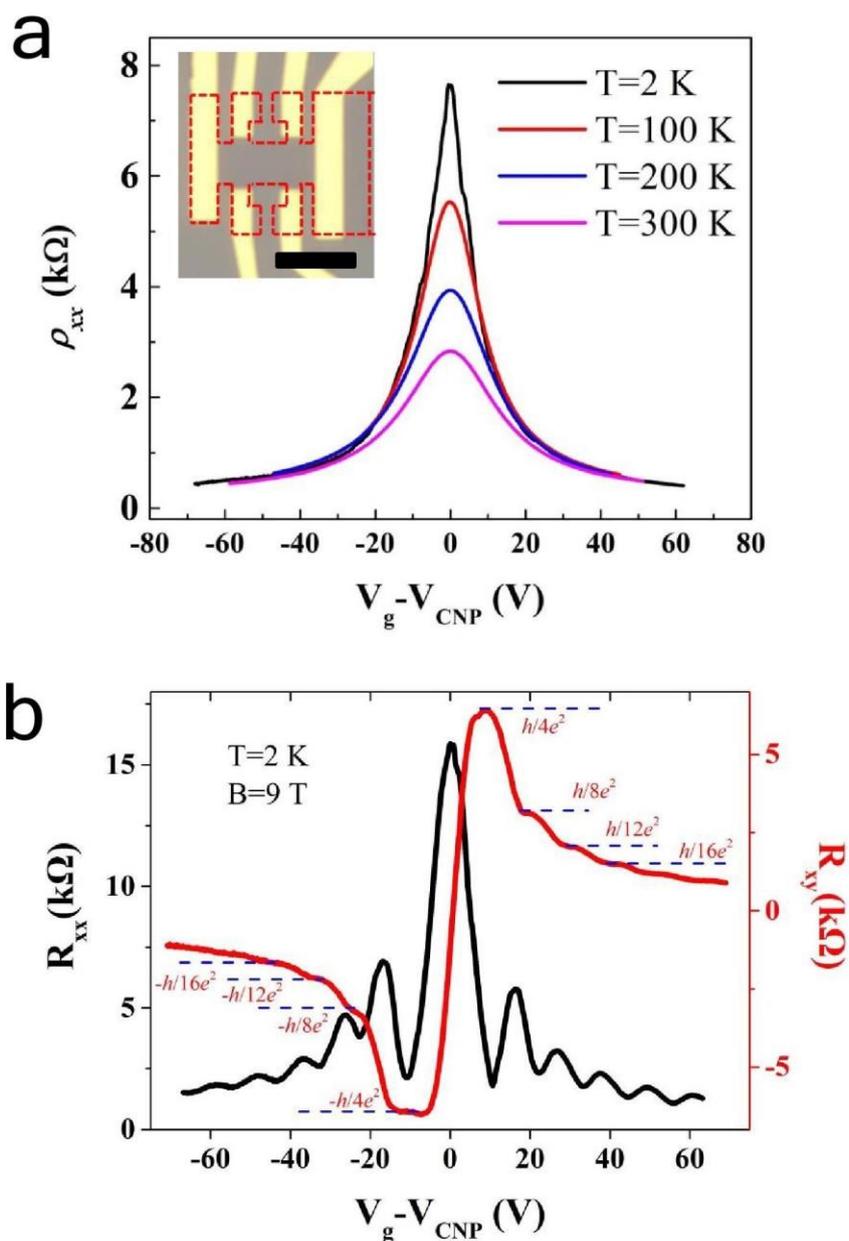
Figure 4 Transport measurement of FET device of bilayer obtained by controlled oxidation.(a) Transport curve of nucleus-based FET device at 2, 100, 200and 300K. The inset optical image shows the configuration of device. The shape of hall bar is donated with red dot line. The scale bar in inset is $5\,\mu m$.(b) Quantum Hall measurement at T = 2 K with a perpendicular magnetic field B = 9 T.