Supporting Information for

High Yield Chemical Vapor Deposition Growth of High Quality Large-Area AB Stacked Bilayer Graphene

Lixin Liu,[†,1,4] Hailong Zhou,[†,2] Rui Cheng,[†,1] Woo Jong Yu,[2] Yuan Liu,[1] Yu Chen,[1] Jonathan Shaw,[2] Xing Zhong,[2] Yu Huang,[,1,3] Xiangfeng Duan[*,2,3]*

[1]Department of Materials Science and Engineering, University of California, Los Angeles, California 90095 USA, [2]Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095 USA, [3]California Nanosystems Institute, University of California, Los Angeles, California 90095 USA

[4]Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000, People's Republic of China

[†] These authors contributed equally to this work

[*] To whom correspondence should be addressed. E-mail: xduan@chem.ucla.edu, yhuang@seas.ucla.edu

1. Bilayer graphene dependent on the position of Cu substrate

A 1.5 × 6.0 cm strip of Cu foil was inserted into the quartz tube. After growth at 1050 °C with H_2/CH_4 ratio of 40 under 5 mbar for 1 hour, the graphene was transferred onto Si substrates with 300 nm SiO_2. We noticed different morphologies and coverage of bilayer graphene grown downstream along the Cu foil as shown in

Figure S1. Large gaps (lightest color) between monolayer domains correspond to uncovered Cu catalyst on the upstream end of the Cu foil. Width of the gaps decreases quickly along the distance from the upstream end, and disappears after ~ 5 mm distance, that is, the rest of the Cu foil is totally covered by monolayer and bilayer domains. Coverage of the bilayer graphene first decreases quickly and then remains nearly stable (Figure S2) because of non-uniform distribution of the carbon fragments source come from the upstream uncovered Cu foil.

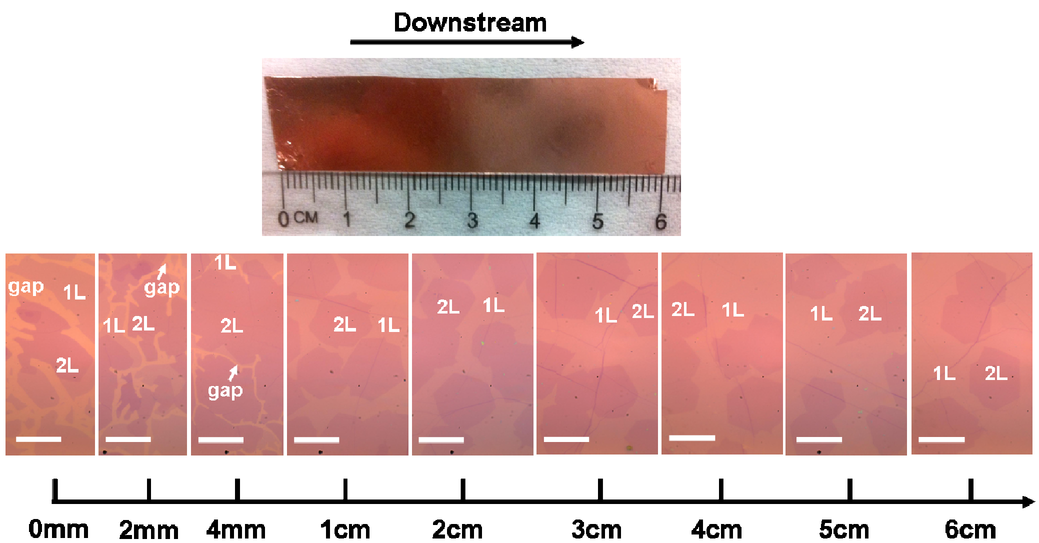

Figure S1. The upper picture is photographic image of a Cu foil strip (1.5 × 6.0 cm) with bilayer graphene. The lower pictures are a series of OM images of graphene along the different positions of the Cu foil starting from upstream end. Scale bars are 20 µm. Uncovered Cu surface (gap), monolayer (1L), and bilayer (2L) graphene are clearly visible on the upstream end, and the gaps disappear starting ~ 5 mm length from upstream end.

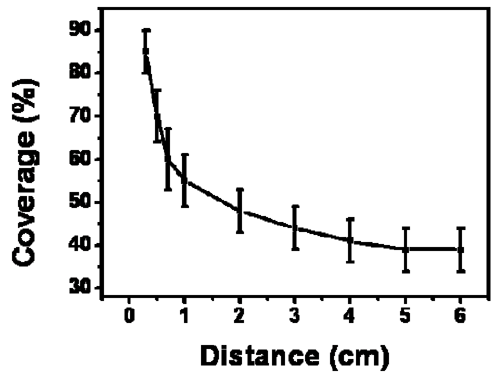

Figure S2. Bilayer graphene coverage as a function of the distance from the upstream end of the Cu substrate.

2. Bilayer graphene coverage dependent on growth time

Figure S3 presents images regarding time dependence of graphene coverage on the center of Cu foils at 1050 °C with H_2/CH_4 ratio of 40 under 5 mbar. The monolayer domains show six-fold lobe-like structure after 2 min growth, and quickly merge together after 5 min growth, and then reach ~ 100 % coverage on Cu substrate after 15 min growth. The bilayer graphene keeps the symmetrical hexagonal shape growth and the coverage of the total area increases from < 1 % to ~ 100 % with increasing growth time from 2 min to 3 hours. The domain density of bilayer is kept nearly constant at ~ 1200 /mm^2, independent of the growth time.

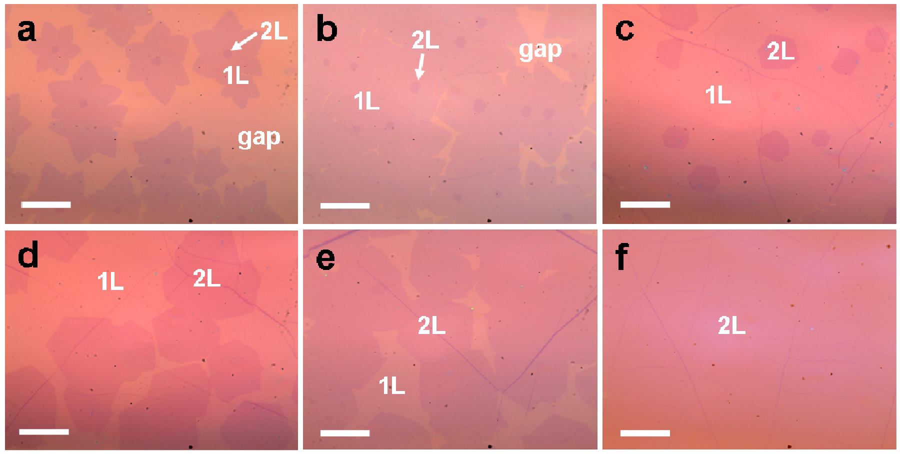

Figure S3. OM images of graphene synthesized at 1050 °C with H_2/CH_4 ratio of 40 under 5 mbar at different growth stages: (a) 2 min; (b) 5 min; (c) 15 min; (d) 1 hour; (e) 2 hours; (f) 3 hours; scale bars are 20 μm.

3. Systematically tuning experimental parameters

The ratio of H_2/CH_4 was tuned from 4.2 to 2666 under 5 mbar at 1050 °C for 2 hours. Optical images of Figure S4 show that the monolayers fully cover the substrates, and the bilayer domains always keep hexagonal shape with different density and size when tune the H_2/CH_4 ratio. The coverage variation curve of the bilayer is shown in Figure S5. It can be seen that the bilayer coverage > 40 % in a very large range of H_2/CH_4 ratio around 20-1400, and decreases dramatically only at both ends of the curve. That is, bilayer graphene can not be easily deposited due to the self-limiting effect of growth graphene on Cu foil when H_2 and CH_4 in the same order of magnitude ($H_2/CH_4 < 20$), which consistent with the previous reports.[4,5] At the same time, the bilayer graphene growth can be suppressed by introducing excessive amounts of H_2 into the chamber ($H_2/CH_4 > 1400$).

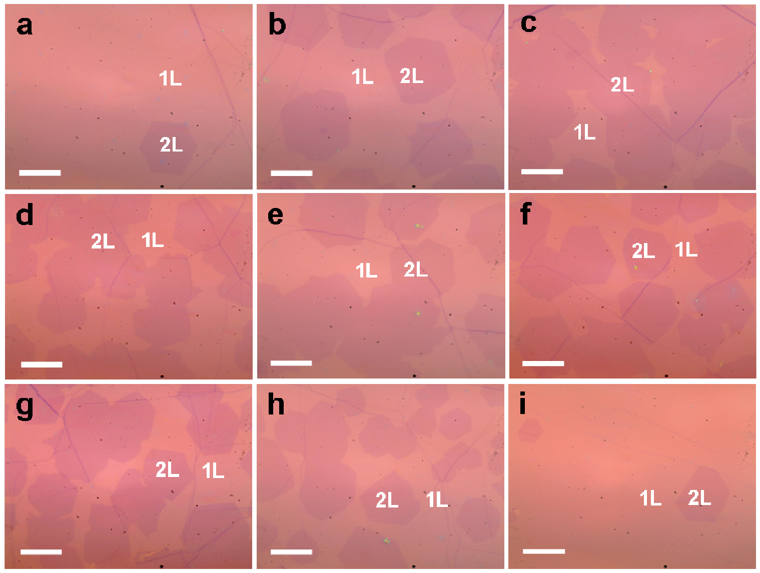

Figure S4. Optical images of graphene transferred onto 300 nm SiO_2 obtained at different H_2/CH_4 ratio: (a) 4.2/1; (b) 25/1; (c) 40/1; (d) 66/1; (e) 166/1; (f) 333/1; (g) 666/1; (h) 1333/1; (i) 2666/1; scale bars are 20 μm. Monolayer (1L) graphene have full coverage of the Cu substrates, darker contrast of hexagonal bilayer (2L) domains on monolayer have different density and size.

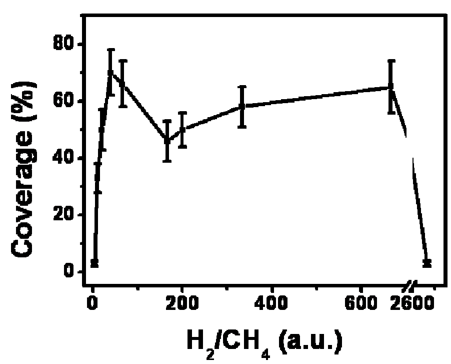

Figure S5. Plot shows coverage of bilayer graphene on the center of Cu foil relative to the ratio of H_2/CH_4.

Then, to examine the effect of growth temperature on epitaxial bilayer graphene, the Cu substrates were first annealed at 1050 °C with Ar/H_2 mixed gas for 30 min, after which the graphene was grown at different temperatures (990 °C, 1010 °C, 1030 °C, 1050 °C) under pressure of 5 mbar with a H_2/CH_4 ratio of 40 for 1 hour. The changes of morphology and coverage of bilayer graphene are shown in Figure S6. Nearly all the monolayer graphene have a full coverage of the Cu substrate. The coverage of bilayer graphene increases from ~ 10 % to ~ 45 % with increasing the growth temperature from 990 °C to 1050 °C, while the density of the bilayer domain decreases when increases the growth temperature (from 2600 /mm^2 to 1160 /mm^2). Therefore, a relatively higher temperature (1050 °C) is a better choice.

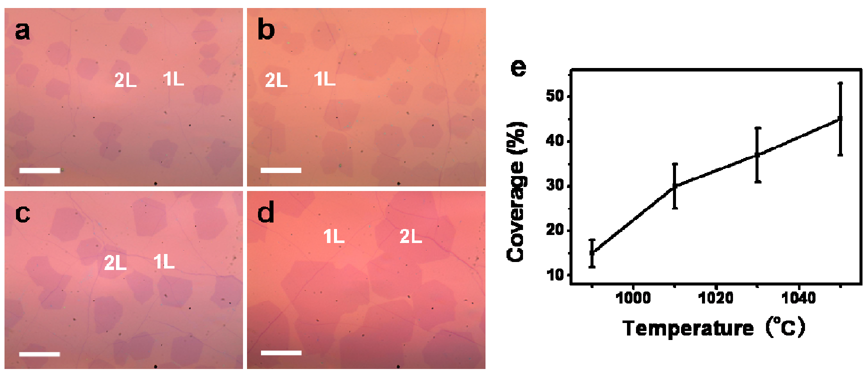

Figure S6. Optical images of graphene transferred onto 300 nm SiO_2 obtained at different growth temperatures: (a) 990 °C, (b) 1010 °C, (c) 1030 °C, (d) 1050 °C; scale bars are 20 μm. All the monolayer (1L) graphene has ~ 100 % coverage. (e) Coverage of bilayer (2L) graphene on the center of Cu foil relative to the growth temperature.

Finally, the growth pressure was tuned from 1 mbar to 100 mbar; the optical images are shown in Figure S7. Bilayer graphene domains on full coverage monolayer keep hexagonal shapes with domain density nearly unchanged. Coverage of the bilayer increases firstly and then decreases with increasing the growth pressure (Fig. S8). On the contrary, AB stacking ratio of the bilayer decreases from ~ 95 % to a relatively low ratio of ~ 65 % with the increasing pressure. For CVD bilayer graphene growth, it is desirable to have a high coverage and high AB stacking ratio. While the AB stacking ratio is always around 65 % when tuning the growth temperature and H_2/CH_4 ratio under pressure of 5 mbar. Therefore, we further studied the influence of growth temperature and H_2/CH_4 ratio on the bilayer AB stacking ratio under 1 mbar. What we observed is that the AB stacking ratio can be increased with increasing growth temperature (Fig. S9), and is almost independent on the H_2/CH_4 ratio. That is, high temperature and low pressure can yield a high AB stacking ratio bilayer graphene.

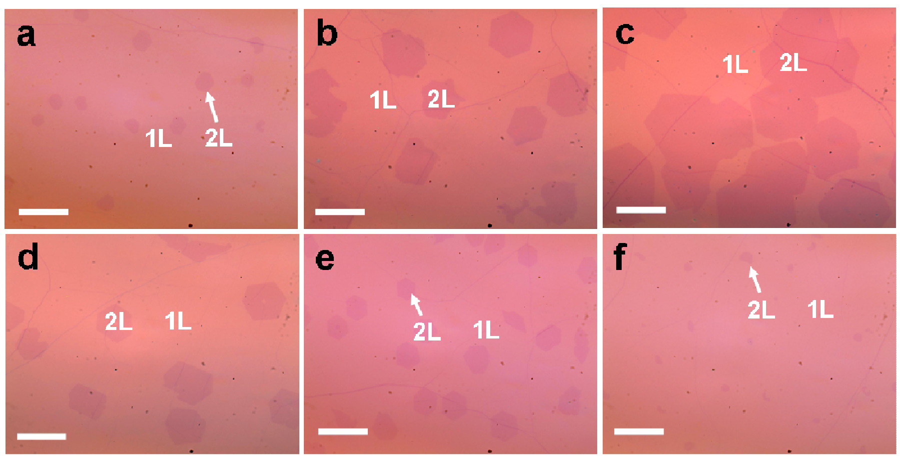

Figure S7. Optical images of graphene under different growth pressure: (a) 1 mbar; (b) 2 mbar; (c) 5 mabr; (d) 10 mbar; (e) 20 mbar; (f) 100 mbar; scale bars are 20 μm. Darker contrast of hexagonal bilayer (2L) domains locates on lighter monolayer (1L).

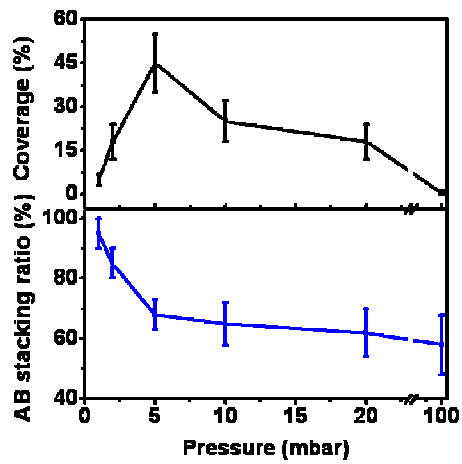

Figure S8. Summary of the bilayer graphene coverage and AB stacking ratio as a function of the growth pressure.

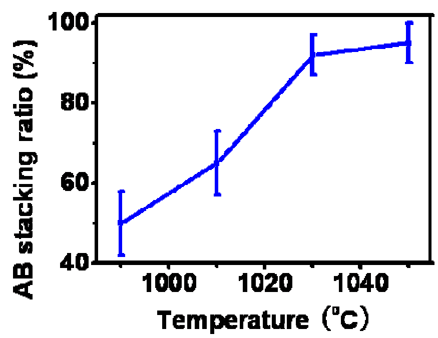

Figure S9. Plot shows AB stacking ratio as a function of growth temperature with H_2/CH_4 ratio of 40 under pressure of 1 mbar for 1 hour growth.

4. Scanning Raman imaging

Scanning Raman imaging was employed to further confirm the AB-stacking bilayer graphene. A color contrast in the optical microscope image of the graphene transferred onto a Si/SiO_2 substrate shows wrinkles, monolayer and bilayer regions (Figure S10a). The 514 nm laser excited Raman spectra were obtained on the single layer and AB-stacking bilayer regions with the typical D (~ 1350 cm^{-1}), G (~ 1580 cm^{-1}), and 2D (~ 2680 cm^{-1}) bands (Figure S10b). The spectra of monolayer graphene (black circle) and AB-stacking bilayer (red circle) show the representative features similar to previous report [4]. Interestingly, we also observe another type of spectrum (*e.g.*, blue circle area) with both the G and 2D peaks nearly double of the intensity of AB stacked bilayer graphene. Nonetheless, the 2D band FWHMs of ~ 64 cm^{-1} and I_G/I_{2D} peak ratio of ~1.15 suggest that this region is also AB-stacked bilayer graphene, although the extra signal intensity requires further investigation. Based on the Raman mapping of G and 2D band, the overall coverage of AB stacked bilayer graphene is estimated to be 91%.

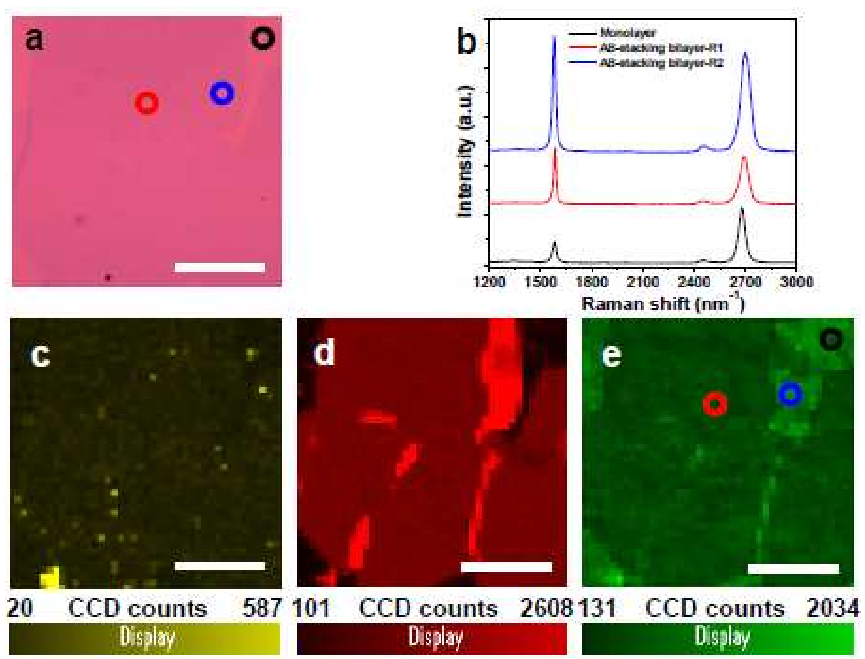

Figure S10. (a) Optical microscope image of graphene transferred onto Si/SiO_2 (300-nm-thick SiO_2) showing wrinkles, monolayer and bilayer regions, scale bar is 20 µm. (b) Raman spectra obtained from the marked spots with corresponding colored circles in (a) and (e). (c to e) Raman maps of the D (1350 cm^{-1}), G (1580 cm^{-1}), and 2D (2680 cm^{-1}) bands, respectively (Renishaw 1000, laser = 514 nm, the Raman map pixel size is 1.5 µm, 50× objector). Scale bars are 20 µm.

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