Chemical vapor deposition growth of large single-crystal bernal-stacked bilayer graphene from ethanol

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A B S T R A C T

Using ethanol as a precursor, single-crystal bilayer graphene domains with dimensions up to hundreds of micrometer, one of the largest reported so far, were synthesized on Cu foils by chemical vapor deposition (CVD). Raman spectroscopy analysis revealed that the bilayers are homogeneously AB-stacked, with very low D-band intensity. Selected area electron diffraction analysis also confirmed the bernal stacking order and the large area crystallinity. Surprisingly, decreasing ethanol pressure in CVD shows an unambiguous tread from self-limited single layer to a multi-layer graphene, and there exists a narrow window of ethanol pressure which is preferred for the formation of large domain bilayer graphene. This suggests the dual effect of ethanol in graphene growth and demonstrates that the formation of different layers of graphene can be controlled by carefully tuning single parameter: ethanol pressure.

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1. Introduction

Graphene, an sp^2-bonded mono-layer carbon material, has been drawing enormous attention due to its extraordinary mechanical, thermal and electrical properties. Chemical vapor deposition (CVD) provides a reliable and consistent method for the synthesis of large-scale single-layer graphene (SLG) [1–5]. In the past few years, many efforts have been focused on enlarging the sizes of single-crystal graphene domains [6–12], in order to avoid the drawbacks brought by the existence of grain boundaries [13,14]. To achieve this, researchers focused on reducing the partial pressure of the carbon source, tuning the C:H ratio, smoothing the Cu surface, as well as adjusting oxygen content of Cu substrates [10–12]. As a result, single-crystal SLG of millimeter or even centimeter sizes were synthesized. Recently, we found that by using ethanol as the precursor, the growth of single-crystal on polycrystalline Cu substrates can be realized through a very simple procedure, and graphene single crystals as large as 5 mm were synthesized [15].

However, the zero band-gap in SLG makes it unsuitable for many applications such as the channels in field effect transistors, despite its high carrier mobility. Recently, several groups reported that a bandgap up to 250 meV can be opened by an external electric field in AB-stacked bilayer graphene (BLG) [16,17]. CVD synthesis of continuous polycrystal AB-stacked BLG has been reported, but the size of single-crystal domains are very small compared with SLG. Besides, in order to break the self-limiting process of SLG on Cu surface, these previous works employed complicated pre-treatments or designed CVD process [18–23], such as spatially arranged Cu substrates [18,21], percentage-engineered Cu–Ni alloy as substrates [19,22], carefully adjusted nucleation pressure of methane [10,20], and nonisothermal growth procedure with variable temperatures [23]. In our previous work, we've shown that when using ethanol as a precursor, simply by extending the CVD growth duration, the self-limiting behavior of SLG on Cu can be broken, resulting in a layer-by-layer epitaxial growth of equilibrium AB-stacked BLG [24]. However, the domain sizes in that case were a few micrometers and growth of large (e.g. over hundred micrometer) domain sized AB-stacked BLG remained challenging. Here, using an improved alcohol catalytic CVD (ACCVD), we report a successful preparation of single-crystal AB-stacked BLG with sizes up to 450 μm, which is so far the largest AB-stacked BLG reported. Balancing ethanol's etching and growth effect through adjusting

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the CVD pressure is found to be critical for the formation of large BLG flakes.

2. Experimental methods

Single-crystal BLG was synthesized using alcohol catalytic chemical vapor deposition (ACCVD), which is similar to the procedure used in the synthesis of single-crystal SLG [15]. A home-made thermal CVD system was employed, with a quartz tube as the reaction chamber. Commercial copper foils (Nilaco Corp., CU-113303) were cleaned using IPA, acetone, and HCl, and heated in air on a hot plate at about 250 °C to oxidize the Cu surface. Afterwards, the foil was folded into a Cu pocket, loaded into the CVD chamber, and placed at the center of the furnace. Then the system was vacuumed to approximately 25 Pa by a mechanical pump for 10 min to remove air from the system. The CVD chamber was heated to the reaction temperature (1065 °C) with an Ar flow (300 sccm) under the pressure of 450 Pa. After reaching 1065 °C, the Ar flow was replaced by a 300 sccm flow of 3% H_2 diluted in Ar (partial pressure of H_2 is 10 Pa), and a 0.06 sccm ethanol vapor flow was also introduced into the system to initiate the growth. The total pressure is kept at 450 Pa, which is the key parameter compared with the CVD conditions for the synthesis of larger single-crystal SLG, since a small variation of the total pressure may result in a much lower yield of BLG, and this will be discussed in detail later. It would take 15–18 h for the formation of 2nd layer graphene with sizes of hundreds of microns, and approximately 20–22 h for the full coverage of bilayer graphene.

The transfer of graphene is conducted using a wet-etching process with poly (methyl methacrylate) (PMMA) as the mediator, as has been explained in many previous works. For transfer to transmission electron microscopy (TEM) grids, the PMMA is removed by a 20-h annealing in the environment of H_2/Ar at 400 °C.

3. Results and discussion

After the growth of 18 h using the conditions in Fig. 1-a, we transfer the graphene to Si/SiO$_2$ substrate, and directly observe the BLG using an optical microscope, since in this way the contrast between SLG and BLG is very strong. Nearly full coverage of SLG is made, and the BLG hexagons are clearly observed, as shown in Fig. 1-b and c. Most of the BLG hexagons are of the edge-to-edge sizes of few tens to few hundreds of μm after an 18 h growth, with an average size ~200 μm. There is a vague trend that the sizes of bilayer hexagons are larger where the nuclei are denser. This size distribution is probably caused by the unevenly distributed nucleation-preferred sites, and hence the different time needed before single-layer graphene merges in to a large polycrystal piece, since expansion of the second layer mainly occurs after the first layer merge into a continuous film. Nonetheless, more than 20% of the flakes are larger than 300 μm and a 450 μm (one of the largest among them) BLG region is shown in Fig. 1-d.

Fig. 1-f shows the Raman spectra of four randomly selected points in Fig. 1-e, and they show Raman features of AB-stacked BLG, including a FWHM value of ~55 cm^{-1}, a 2D peak position at ~2710 cm^{-1} (about 10 cm^{-1} up-shift compared with SLG), and that the intensity ratio of 2D to G is ~1. No obvious D band can be observed in these locations, indicating that the defect level is very low.

To demonstrate the homogeneity of the BLG area, we plot Raman maps of the 2D/G ratio, the full width at half maximum (FWHM) of the 2D peak, and the position of the 2D peak (Fig. 2a–c). In all three maps, the contrasts between the BLG area and the SLG area are very strong. Except for contaminations on the graphene film which were brought by the transfer procedure, the color on the BLG area in each map is very homogeneous, indicating the quality of the BLG is homogeneous. Fig. 2-d shows an optical image of a BLG grown by flowing 12 h ^{12}C ethanol, followed by 2 h ^{13}C ethanol. Intensity plot of ^{12}C G band (locating at approx. 1588 cm^{-1}) and ^{13}C G band (locating at approx. 1528 cm^{-1}) of this sample is shown in Fig. 2-e, which reveals a clear enrichment of ^{13}C at the edge of the second layer in a BLG. This also confirms that the second layer in our BLG slowly grows when the first layer completely formed. Meanwhile, some red dots in Fig. 2-e implies that, though growth of ^{13}C mainly occurs at edge of the second layer, some exchange of carbon atoms in the as-grown area also happens. This may be
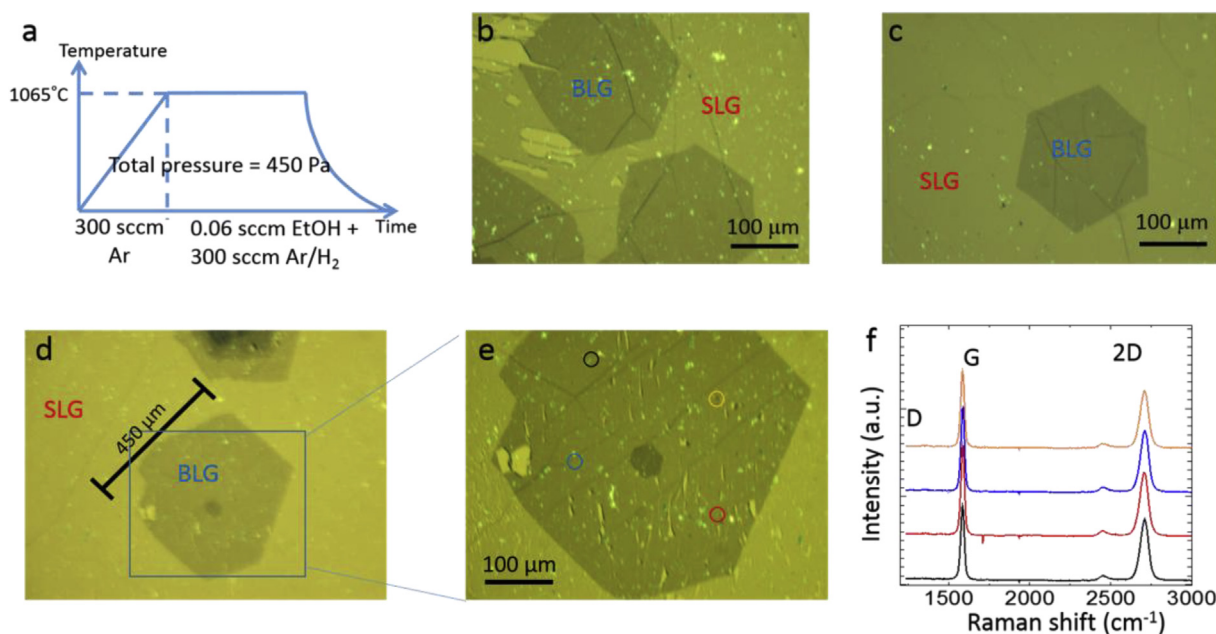

Fig. 1. a) CVD conditions of the growth procedure. b) and c) Microscopic images of BLG on Si/SiO$_2$ substrates. d) and e) Microscopic images of a 450 μm BLG hexagon. f) Raman spectra of four random locations as marked in e). (A colour version of this figure can be viewed online.)