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Towards wafer-size strictly monolayer graphene on copper via cyclic atmospheric chemical vapor deposition

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ABSTRACT

Here we employ cyclic atmospheric chemical vapor deposition method to readily achieve strictly monolayer graphene continuous sheet with size as large as several square centimeters on copper foil. The uniformity and quality of as-synthesized graphene sheet have been verified by optical microscope, Raman, and electronic measurement, etc. The mechanism of this method is also revealed by carbon isotope growth and following Raman mapping analysis. This simple but effective strategy is promising to be extended into mass production in future.

1. Introduction

Uniform and large area graphene sheet is vital for graphene related sophisticated applications including electronics, optoelectronic and mechanics etc. As we know, chemical vapor deposition (CVD) is the widest adopted fabrication method for large scale high-quality graphene sheet, which generally conducts on the basis of copper foil due to the ease growth of monolayer on copper as well as the low cost of copper foil [1]. However, it is still a challenge to synthesize large scale strictly monolayer (or uniform) graphene sheet due to the co-existence of epitaxial and self-limiting growth mechanism on copper or other metal substrates [2]. To solve this problem, many improved growth strategies or alternative substrates have been employed, including large sized single crystal graphene growth [3,4], transition metal substrate growth [5,6], liquid metal [7,8] and binary metal alloy substrate growth [4,9], etc. Fairly speaking, these improvements or novel strategies realized the goal in some degree but at the expense of drastic increasing complexity or high cost. In other words, it is less likely for these methods to be adopted by mass production in future.

Here we report a simple but effective strategy to achieve large-sized uniform monolayer graphene on commercial polycrystalline copper foil in which we only linked several, generally two, conventional atmospheric CVD growth processes spaced by a short time hydrogen etching operation. Therefore, this novel method neither enhances the complexity of growth nor increases the energy or resource consumption. Generally, strictly monolayer graphene sheet with size of several square centimeters can be readily achieved with this novel method. In principle, there is no limit on the scale of strictly monolayer sheet, which mainly depends on the dimension of instrument for growth. The uniformity of monolayer graphene has been verified by optical microscope and Raman. Moreover, the high quality of graphene has been confirmed by transmission electron microscope (TEM), selected area electron diffraction (SAED) and electronic measurement. Importantly, we have discussed the possible mechanism for the elimination of few layers structures (FLS) during the hydrogen etching and following growth processes. The removal of FLS during hydrogen etching is attributed to the highly reactivity of defects, such as metal step [10] or nanoparticles in FLS central [11]. In the following growth, the regrowth of graphene is very likely to epitaxially grow along the edge of etched graphene rather than form new nucleuses on fresh copper surface. This phenomenon stems from that grain edge has a much lower growth barrier than forming new nucleuses and additionally, the reconstruction of exposed copper surface further suppress the nucleation of grains as well. It is worthy to mention that similar growth-etching-regrowth strategy had been adopted to suppress the nucleation density of graphene grains or construct epitaxial heterostructures [12–14]; however, here we **for the first time** employ it to remove the FLS in a continuous graphene sheet to achieve large scale strictly monolayer graphene sheet.

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2. Experimental methods

2.1. Strictly monolayer graphene synthesis

For the 1st grown graphene, we synthesize continuous graphene sheet on commercial copper foil (Alfa Aesar, stock no. 13382, we also employed another two types of copper foil to verify this method, that is, Alfa Aesar, stock no. 46365 and copper foil from local manufacturer) in 1 inch quartz tube. 350 sccm Ar is employed to expel air in system and then 16 sccm H_2 is introduced to anneal copper under 1050 °C for ~30 min. After that, 15 sccm diluted CH_4 (1000 ppm in Ar) is introduced and maintained for ~ 10 min for graphene growth. Finally, the supply of CH_4 and power of furnace are shut down and the whole system is fast cooling under the mixture of Ar and H_2. For the 2nd grown graphene, we do not cool down the system after stopping the supply of CH_4 but maintain the system under 1050 °C for a certain time, then the supply of CH_4 is restored and maintain for another 10 min to repair etched graphene sheet.

2.2. Device fabrication

Regrown graphene sample is transferred from copper to 300 nm SiO_2/Si wafer by electrochemical method and then patterned by electron beam lithography (EBL) and plasma etching. After that, electrodes patterns are designed and fabricated by EBL and then filled by 10 nm Cr/50 nm Au as contact electrodes. All the PMMA is removed by acetone rinse.

2.3. Characterizations

SAED pattern and high resolution monolayer morphology of sample is conducted by TEM (Tecnai G2-20, FEI). Single point Raman and carbon isotopes mapping are collected in a confocal Raman/PL system (HR-800, HORIBA Jobin Yvon) and the 2D Raman mapping is done by WITec (Alpha 300 RS+). The electrical measurements are carried out at room temperature with a Keithley 4200 in a probe station (CRX-6.5K, Lake Shore).

3. Results and discussion

The whole growth process for strictly monolayer graphene is simple and effective. As shown in Fig. 1a, here we just linked two conventional CVD growth procedures into one growth.

First, we conduct a conventional CVD growth to achieve a continuous graphene sheet in the environment of Ar, H_2 and CH_4 gases, certainly, there are a large number of FLS doped in the sheet as can be seen in Fig. 1b, denoted as 1st grown graphene. Then, the carbon source, CH_4, is turned off but the flows of H_2 and Ar are maintained for several minutes to etch FLS. As well known, it is inevitable for the presence of inherent defects in CVD-grown graphene sheet [15], thus, etching pores originated from these inherent defects [16] would appear readily in monolayer sheet when exposed in reactive condition (Fig. 1c). It should be noted that the exact etching time depends on detailed growth condition. In our case, the etching time is ~10 min (excessive etching would introduce FLS again, Fig. S1) and after that, carbon source is turn on and regrowth process is started, finally, the broken graphene sheet is repaired by regrowth and forms a continuous sheet again (Fig. 1d), denoted as 2nd grown graphene. We only show a relative small scope of transferred 2nd grown graphene on silicon wafer in Fig. 1d. Actually, the size of strictly monolayer graphene sheet (Fig. S2) is much larger than what we shown here, confirming the large scale uniformity of as-synthesized graphene sheet. Importantly, the whole growth process has not introduced any external items like special substrates or accessories; besides, we also have tried this novel method on various copper foils, similar result can be acquired on all of them (Fig. S3); therefore, it is supposed to be a universal strategy for strictly monolayer graphene growth on copper.

The uniformity of monolayer graphene sheet can further be identified by Raman mapping spectra. The optical image shown in

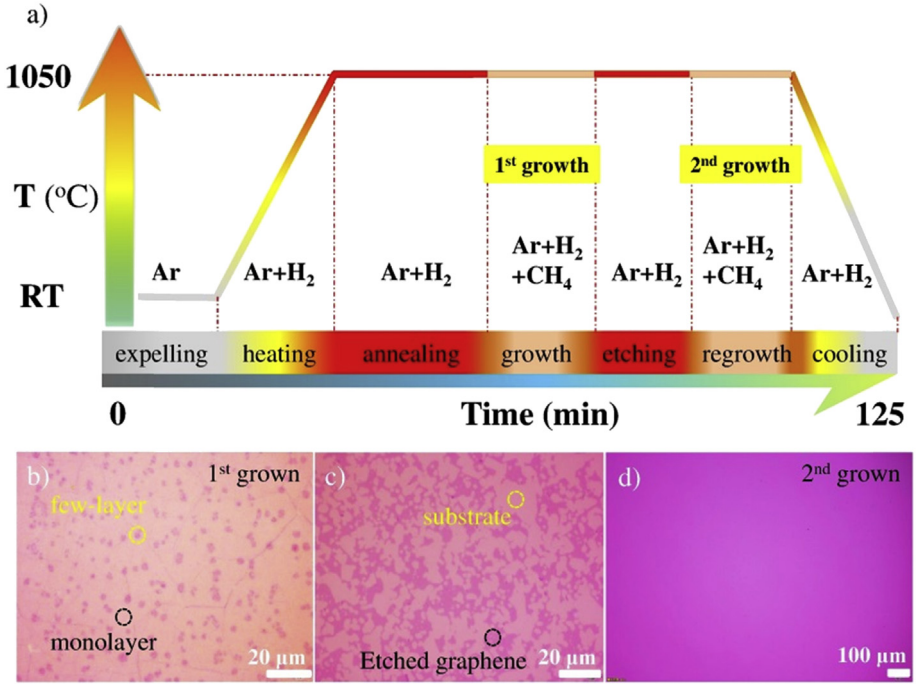

Fig. 1. (a) the schematic of growth procedure; (b–d) optical images for 1st grown graphene sheet, etched 1st grown graphene sheet and 2nd epitaxial grown graphene sheet from the etched edges of graphene, respectively, transferred on silicon wafer. (A colour version of this figure can be viewed online.)