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Synthesis of large size uniform single-crystalline trilayer graphene on premelting copper

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ABSTRACT

Single-crystalline trilayer graphene (TLG) has attracted intensive interest due to rich optical and electronic properties. However, precise synthesis of large-size uniform single-crystalline TLG with ABA stacking still remains enormous challenge. Herein, an atmospheric pressure chemical vapor deposition (APCVD) process was developed to fabricate the uniform single-crystalline TLG on premelting copper at 1080 °C, which is slightly lower than copper melting temperature. As the results, ~80 μm uniform single-crystalline TLG with ABA stacking was achieved on a premelting copper layer. Raman mapping and selected area electron diffraction of individual isolated domains reveals they are uniform single-crystalline with ABA stacking. The growth mechanism of the TLG was explored by studying the influence of varied growth temperature, which is subsequently shown that the 2nd and 3rd layer graphene grow simultaneously from external to internal with a twist angle of 20 ± 5°.

1. Introduction

It has been demonstrated that the properties of graphene greatly depend on layer number [1–5]. Single layer graphene (SLG) has semimetallic properties and zero-energy band gap structure, limiting its application in semiconductor industry [6]. Bilayer graphene (BLG) has been theoretically [7] and experimentally [8] proved to have a band gap which is continuously tunable in a perpendicular electric field, providing opportunities for graphene in optoelectronic devices [9]. For trilayer graphene (TLG), two stable crystallographic configurations are reported: ABA and ABC stacking order [10–12]. ABA-stacked TLG are semimetals with an electrically tunable band overlap [4,13,14], while ABC-stacked TLG are more like semiconductors with an electrically tunable band gap [13,15], which means TLG have more extensive application than SLG and BLG. Therefore, synthesis of large single-crystalline trilayer graphene would provide a material with both fundamental interests and practical application.

Chemical vapor deposition (CVD) on copper is considered the most promising method [16,17] to achieve large-size single-crystalline graphene among all of the synthesis methods because of high yield and high quality [18]. In typical CVD graphene method on copper, it's considered that graphene growth on copper is controlled by the self-limited process [17]. However, in recent years, more and more studies have demonstrated the self-limited process on copper cannot be applied in many cases [19–21]. Millimeter-scale single-crystalline monolayer and bilayer graphene have been achieved on copper successively [8,22–24]. For bilayer and few layer graphene, the most common growth model was proposed as an inverted wedding cake model [25,26]. The 2nd and 3rd layer graphene usually has smaller size than the 1st layer graphene [27]. Tour et al. reported synthesis of inverted wedding cake bi- and trilayer graphene with trilayer graphene domain of ~30 μm by controlled pressure chemical vapor deposition (CP-CVD), whose growth mechanism was underlayer growth [27,28]. It was explained the 2nd layer graphene grown below the 1st layer as the diffusion of carbon atoms through the Cu bulk to the Cu surface.

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Chiu et al. achieved inverted wedding cake ABA stacking trilayer graphene with the domain of ~30 μm, whose growth mechanism was penetration mechanism [29,30]. They explained CH_x could diffuse through the defect holes of the upper layer graphene to form the 2nd and 3rd layer. Zhai et al. grown AB stacking bi- and trilayer graphene with size of 80 μm and 50 μm on oxidized copper which was the largest at that time [31]. However, the feature of graphene flakes synthesized by all the above methods is the coexistence of mono-, bi-, and trilayer graphene rather than a uniform trilayer graphene. Here, we report a process to achieve a uniform ABA-stacked single-crystalline TLG with larger size on premelting copper via APCVD. The effort for understanding the growth mechanism of the uniform TLG has also been taken in this current study.

2. Experimental detail

2.1. Preparation of graphene

A home-made hot wall APCVD system with quartz tube furnace was used to fabricate graphene. A vacuum background of about 10 Pa was reached in the tube before graphene growth. A 25-μm-thick copper foil (Civen International Inc., 99.99%) with size of 40 × 40 mm was used as substrate. Ultrasonic cleaning for copper foils with glacial acetic acid (AR), acetone (AR) and DI water was conducted for 20 min to remove oxides and contaminations on the surface of the foil. The copper foil was placed on a quartz boat whose position was controlled by a dragger (Fig. 1). The copper substrate was shifted to the spot of 50 cm and heated up to 1080 °C within 70 min at atmospheric pressure with 500 sccm Ar (99.999%) and 100 sccm H_2 (99.999%). The furnace was heated then kept at 1080 °C for 90 min to coarsen the grain size of copper foil with and 300 sccm H_2. Subsequently, the foil was passivated at 1080 °C with 500 sccm Ar and 3 sccm O_2 (99.999%) for 10 min. Graphene was deposited at 1020–1080 °C under a flow of 500 sccm Ar, 300 sccm H_2 and 1.2 sccm CH_4 (99.999%) for 1 h. After growth, the copper was shifted to the position of 10 cm for cooling freely. Meanwhile, Ar and H_2 were kept at 500 and 100 sccm respectively, whereas CH_4 was turned off. The procedure was shown in Fig. 2 in detail.

2.2. Transfer of graphene

For further characterization by optical microscopy, raman spectroscopy and high resolution transmission electron microscopy (HRTEM), the as-grown graphene on the copper were transferred onto a p-doped Si substrate with 300 nm SiO_2 layer (KMT Corporation) or a TEM grid (Beijing Zhongjingkeyi Technology Co., Ltd., GIG-2020-300) by a traditional wet chemical transfer method [32].

Copper foil was cut into pieces 10 × 10 mm in size. Then, a thin layer of 4 wt% polymethyl-methacrylate (PMMA, 950 k molecular weight) was dissolved in Anisole (AR) and spin-coated on one side of graphene/Cu, following by baking at 150 °C for 10 min in air. Meanwhile, the other side of copper foil was treated by saltpeter solution (HNO_3: H_2O = 2: 6) for 10 min. The PMMA/graphene/Cu was then floated over 1 mol/L $FeCl_3$ (AR) solution for 3 h to remove the Cu substrate, and then transferred to hydrochloric acid solution (HCl: H_2O = 1: 10) and DI water for 30 min respectively to further remove the remained metal ion. The PMMA/graphene was scooped up with SiO_2/Si wafer or a TEM grid and dried in a desiccator at room temperature for 3 h. After drying, the PMMA/graphene was heated on a hot plate at 150 °C for 10 min to promote the adhesion between graphene and substrate. Then, the PMMA/graphene/Substrate was dipped in acetone at 60 °C for 1 h to remove PMMA. Finally, the graphene/Substrate was vacuum annealed at 150 °C for 5 h to further remove organic residues.

3. Characterization

Raman spectroscopy was recorded at room temperature using a Horiba LabRam HR800 Ev with laser excitation at 532 nm and a power of less than 5 mW. Optical microscopy (OM, MX6RT, Sunny Optical Technology Co.) was directly carried out in a reflection mode without oxidation at 200 °C in air. Scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) were carried out using FEI Quanta-FEG250 at 20 kV. Atomic force microscopy (AFM) imaging was performed using a Bruker Multimode 8 DI in contact mode. High resolution transmission electron microscopy (HRTEM) combined with selected area electron diffraction (SAED) was carried out using a FEI Titan at 200 kV.

4. Results and discussion

After growth at T_{dep} = 1080 °C, hexagonal graphene flakes with a uniform contrast are clearly observed, as shown in Fig. 3a and b. However, a few graphene flakes show a nonuniform color contrast between center and edge, indicating different layer number. Fig. 3c presents the AFM surface morphology of the uniform graphene flake transferred to SiO_2/Si. The height profile across the edge reveals the thickness of the uniform graphene flake is 1.8 nm, which is slightly larger than BLG [33]. The edge of graphene flake

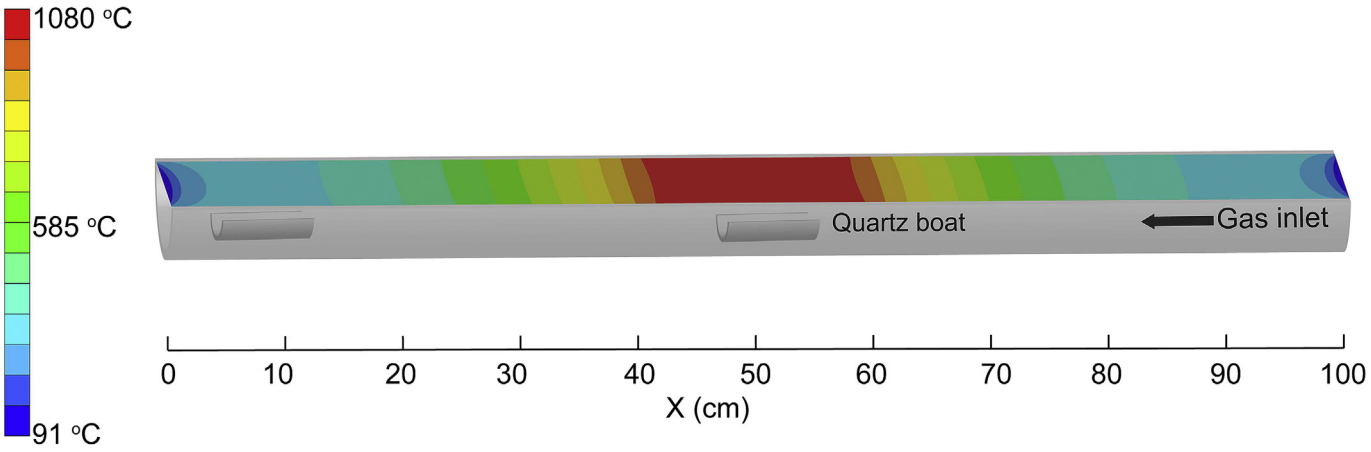

Fig. 1. The temperature field of the CVD system. (A colour version of this figure can be viewed online.)