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Top or underneath? Revealing the structure of multilayer graphene domains with atomic force microscopy and theoretical analysis

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ABSTRACT

The structure of multilayer graphene domains on Cu foil is revealed with atomic force microscopy and theoretical analysis. The phase images of force microscopy enable the separation of the graphene domains from the naked areas of Cu foil. Furthermore, the phase images enable the discrimination of the different graphene layers and structures. For example, some of small graphene layers show a darker phase contrast than the surrounding single layer districts while other small layers have a brighter contrast with respect to the surrounding single layer areas. Then, we proceed to determine whether the few-layer graphene domains are wedding cake (WC) or inverted wedding cake (IWC) structures. The graphene samples with the artificial WC, IWC and sandwich structure were fabricated on Cu through layer by layer method. Based on the results of the artificial structures, we can know that the areas showing darker contrast in the as-grown samples correspond to the WC structure and the areas showing bright contrast are the IWC domains. Theoretical discussions disclose that the different energy dissipated on Cu or the respective graphene layer is responsible for the variation of the phase contrast.

1. Introduction

Since it was isolated successfully for the first time in 2004, graphene has demonstrated many of excellent properties and various promising applications. Scalable synthesis of high quality graphene is critical both to the potential applications of graphene and the fundamental researches on its physical properties. Among all the approaches of acquiring graphene for the electronic and optical purposes, chemical vapor deposition (CVD) on Cu foil is mostly adopted because its obvious superiorities such as top quality next to the mechanical cleavage graphene, time-saving process, acceptable producing cost and good controllability of product structures. To date, sorts of graphene structures have been synthesized on Cu foil under the different parameters, from monolayer to bilayer, trilayer and few layers; from large-size sheet to triangular, square, hexagonal, twelve-pointed and snow-like domains; from perfect Bernal to rotated stacking structure [1–4]. Characterizing the structure of graphene samples plays a key role in learning the complicate growth mechanism during the CVD process and analyzing the measured properties of the graphene materials.

Comparing to the relative consistent results on the domain size, layer number, and quality of graphene layers, the stacking order between the different graphene layers is still in discussion. Some researches imply that the small-size graphene sheet is on the top of large-size sheet, namely wedding cake model (WC model) [4–12]. In the investigation of the influence of H_2/CH_4 ratio, carbon source, H_2 flow on the formation of graphene multilayers, the authors speculate that the structure of multilayer graphene is WC model [4,5,7,11]. Another research group supports this model also through observing the graphene domains at the different growing time [12]. The second graphene layer is grown successfully on the top of graphene substrate by putting some fresh Cu foils at the upstream of CVD furnace, which serves as an evidence of the WC structure also [9]. And some other structure analysis such as atomic force microscopy (AFM) imaging of the multilayer graphene edges and the Raman measurements on the carbon isotope-labeled graphene indicate that the graphene sheets arrange in WC model too [6,8,10]. However, some studies suggest a different model. They propose that the structure of multilayer graphene is inverted wedding cake model (IWC model), that is to say, the small-size layer is underneath the large-size sheet [13]. Through characterizing the structure of few-layer graphene produced under their particular growing parameters by AFM, electron microscopy, low energy electron diffraction and microscopy, the IWC structure is suggested in the reports [14–18]. Furthermore, the testing results of Raman or

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time of flight secondary ion mass spectrometry on the isotope-labeled graphene advocate the IWC stacking of the used samples as well [19,20]. Some calculation works also explain the reasonableness of the formation of IWC structure [21–23]. The controversies on the structure of multilayer graphene are not a surprise because the growth of graphene is extreme sensitive to the synthesizing parameters. Therefore, the structure of multilayer graphene may vary from growth system to growth system. Even further, we can not suppose that all of multilayer graphene domains on one piece of Cu foil are stacked with the same model. To date, we do not have enough evidence to exclude that the WC and IWC structure can coexist in one sample, which means that the stacking of few-layer graphene may be different from domain to domain. Thus, the importance of discerning the structure of few-layer graphene at single domain level by a facile, labeling-free approach is obvious. Currently, the Raman measurements on the isotope-labeled samples can determine the stacking of graphene sheets. For the non-labeled CVD graphene samples, the Raman results on stacking information are ambiguous. Scanning electron microscopy (SEM) can give few hints of the stacking style either although the layer number can be counted through the contrast difference. The most widely used AFM and other probe microscopes provide fruitful information on the thickness, layer numbers, domain boundaries, frictional and electronic properties of the CVD graphene samples [24–28]. Very few reports have attempted to discern the vertical position of graphene sheets in multilayer domains by AFM imaging except in the reference [10] in which the AFM topography images of the edge of few-layer graphene domains are used as a supporting evidence for the WC model together with the electron microscopy analysis.

In this report, we identify whether the small-size graphene layer is on the top of or underneath the large-size graphene sheet by the contrast showing in the AFM phase images. The changing of the phase contrast is theoretically explained by the different energy dissipated on the corresponding graphene layer. And the phase images of different domains in one sample confirm the coexistence of WC and IWC structures in the same piece of Cu foil (the growth mechanism of these two sorts of structures will be discussed in future work and is beyond the scope of this report). This method is proved to be applicable to the transferred graphene on SiO_2/Si substrate also. Compared to the most adopted isotope-marking methods, the phase imaging of AFM is a robust and easy-to-use way to determine the structure of few-layer graphene at single domain level. This is of crucial importance for inferring the specific growth mechanism at the corresponding position and local micro-environment rather than the single growth way deduced from the statistical results of whole sample in most of current researches.

2. Experiments and methods

Cu foils (99.8%, Alfa Aesar Co.) were treated by several rounds of ethanol, acetone, diluted hydrogen chloric acid and deionized (DI) water and dried completely by N_2 flow before loaded into the CVD furnace. The system was heated up to 1000 °C under the H_2/Ar atmosphere and kept at this temperature for 30 min. Then the temperature was increased to 1070 °C (slight lower than the melting point of Cu) and hold at this temperature for several minutes with 100 sccm of H_2, 200 sccm of pure Ar and 2 sccm of Ar/CH_4 mixing gas (pre-diluted, CH_4, 1% in volume) to prepare the isolated multilayer graphene domains. After that, the system was cool down to room temperature rapidly under the protection of H_2/Ar mixture. To prepare the isolated single layer graphene domains, Cu foils were annealed further at 1050 °C for 3 h after finishing the treatment at 1000 °C while keeping the other parameters same to the synthesis of isolated multilayer domain samples. The large size single layer graphene was synthesized with the same parameters to that of the isolated multilayer graphene domains except the H_2 flow rate is 15 sccm when growing at 1070 °C.

Transferring was performed under the assistance of PMMA film ((Poly(methylmethacrylate), 950 PMMA A4, MicroChem.) through the widely used process [14]. The PMMA film was rinsed away by several rounds of cleaning in hot acetone. After the treatment of hot acetone, the transferred graphene layer was annealed at 360 °C for 3 h in vacuum, and then was taken out after cooled down to room temperature naturally for starting the next step-AFM observation or stacking another graphene layer. For the sandwich structure on Cu, the WC and IWC structure on SiO_2/Si substrate, the samples were annealed with this process also after the transferring of the second graphene layer.

All AFM experiments were carried out on a Ntegra Prima (NT MDT) microscope operating in semi-contact model. The probes were bought from BudgetSensor Co. with the resonant frequency locating at around 300 kHz. The SEM and Raman measurements were conducted on the apparatus from JEOL Ltd. (6701F, 5 kV) and Thermo Scientific DXR (excited at 532 nm) correspondingly.

3. Results and discussion

The as-prepared graphene on Cu foil is characterized by amplitude modulation AFM in the repulsive regime [29]. In the topography image of Fig. 1a, graphene domains cannot be identified because the small thickness of graphene layers is totally screened by the large roughness of Cu foil. However, they are clearly revealed in the AFM phase image of Fig. 1b acquired simultaneously with Fig. 1a. The dark polygons are graphene domains while the uncovered areas of Cu foil show a brighter contrast. Zoomed into small scales, more interesting details about graphene domains are disclosed. The phase image of Fig. 1c (topography image, Fig. S1a) shows that certain areas of graphene domains display different phase contrast. Two dash arrows are superimposed in Fig. 1c to point out two areas with darker contrast. Even more interestingly, we observed that certain areas of graphene domains have medium-bright contrast (the brightness is dimmer than the naked districts of Cu substrate), as the hexagonal area marked out with the solid arrow in the phase image of Fig. 1d (topography image, Fig. S1b). To exclude that the contrast difference in the areas marked out by the dash and solid arrows in Fig. 1c and d is caused by the different experimental parameters, the medium-bright and darker areas are recorded in one single phase image of Fig. 1e (topography image, Fig. S1c). Several solid and dash arrows are added in Fig. 1e to help recognizing these two kinds of areas also. The shape of the areas displaying darker or medium-bright contrast is observed as hexagonal or deformed hexagonal in most of times, showing the typical features of CVD graphene layer. Therefore, we think that the multilevel contrast is caused by the multilayer structure of graphene domains. Additional SEM and Raman experiments were carried out to analyze the samples. In the SEM image of Fig. 1f, the graphene domains demonstrate as dark contrast also. Some areas as shown by the inserted magnification views of the white arrow positions demonstrate deeper contrast than the other part of graphene domains, indicating that these graphene domains are multilayer structure. No medium-bright areas are found in repeat SEM experiments. A Raman spectrum of graphene on Cu foil is given in Fig. S1d. The value of I_{2D}/I_G ranges from around 1 to 3 revealing the variation of the layer number in the different graphene domains, which confirms the coexistence of single and multilayer domains further. Thus, the AFM, SEM and Raman results provide enough evidences to state that the hierarchical contrast observed in the phase images is produced by the multilayer structure of graphene domains.