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Scanning electron microscopy characterization of structural features in suspended and non-suspended graphene by customized CVD growth

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ABSTRACT

We report an improved recipe for synthesizing high quality graphene through chemical vapor deposition (CVD), scanning electron microscopy (SEM) characterization of CVD graphene, and optimized SEM imaging conditions for efficient visualization of surface features in CVD graphene. We have developed an optimized graphene growth recipe by characterizing the quality of as-grown graphene using Raman spectroscopy and SEM. We have examined graphene samples both on copper (Cu) and silicon dioxide (SiO_2) substrate using SEM. We have found that features on the samples are highly sensitive to both SEM imaging conditions and the type of detector used. With low acceleration voltage (1 keV), immersion lenses, and through the lens detector, we have clearly observed fine features including wrinkles, folding lines, defects, and different layer numbers of graphene, many of which are not visible in un-optimized SEM images. Further, we demonstrate mechanical bulging of suspended CVD graphene membranes covering microtrenches by using electron beam to activate the trapped gas underneath. Our findings and techniques can lead to improved characterization, understanding, and manipulation of graphene and other two-dimensional materials.

1. Introduction

Graphene, a two-dimensional (2D) hexagonal carbon crystalline sheet, has attracted extensive attention since its discovery [1]. To date, chemical vapor deposition (CVD) [2,3] holds promise in producing large scale high-quality graphene for industrial applications [3]. Many attempts of growing large area single layer graphene (SLG) have been made. Besides SLG, polycrystalline graphene also has excellent mechanical properties comparable to that of SLG [4]. Moreover, wafer-scale continuous polycrystalline graphene films can be easily grown, showing that polycrystalline graphene has great potential for future applications such as nano- and micro-electromechanical systems (NEMS and MEMS) [5]. For characterizing quality, number of layers, defects, and atomic structures of graphene, many techniques such as atomic force microscopy (AFM) [2], transmission electron microscopy (TEM) [6] and Raman spectroscopy [7] have been employed. Among the many characterization methods, scanning electron microscopy (SEM) is a non-contact, mostly non-destructive, and comparatively more convenient and efficient tool for fast imaging, making it highly attractive for characterizing micro- and nano-scale features of graphene including wrinkles, folding lines, and grain shapes, especially for CVD grown graphene. However, due to its atomically thin structure, graphene is transparent to high acceleration voltage SEM and it has been challenging to make SEM as a powerful tool for imaging graphene, especially at the device level, for engineered graphene structures and devices. Generally, attaining detailed structural features in imaging graphene devices has been more difficult than in devices made of more conventional materials or structures (e.g., nanowires, top-down lithographically defined NEMS devices) [8,9].

In this work, we have examined a set of varied CVD growth experiments to synthesize high quality and continuous graphene on copper (Cu) foils. The resulting films are carefully measured and compared to identify optimal growth parameters. Then, together with Raman spectroscopy, SEM imaging has been conducted on both suspended and non-suspended CVD graphene. We provide insight into the best set of imaging parameters for characterizing graphene features using SEM by comparing SEM images with different operating conditions, namely, electron energy and type of detectors, for different graphene structural features.

2. Graphene growth on Cu

We performed graphene synthesis with a home-built chemical vapor deposition system (Fig. 1). Using this system, a variety of CVD growth recipes have been explored to yield uniform and continuous large area graphene films. The resulted samples have been characterized using Raman and SEM observations, to establish optimized CVD growth parameters.

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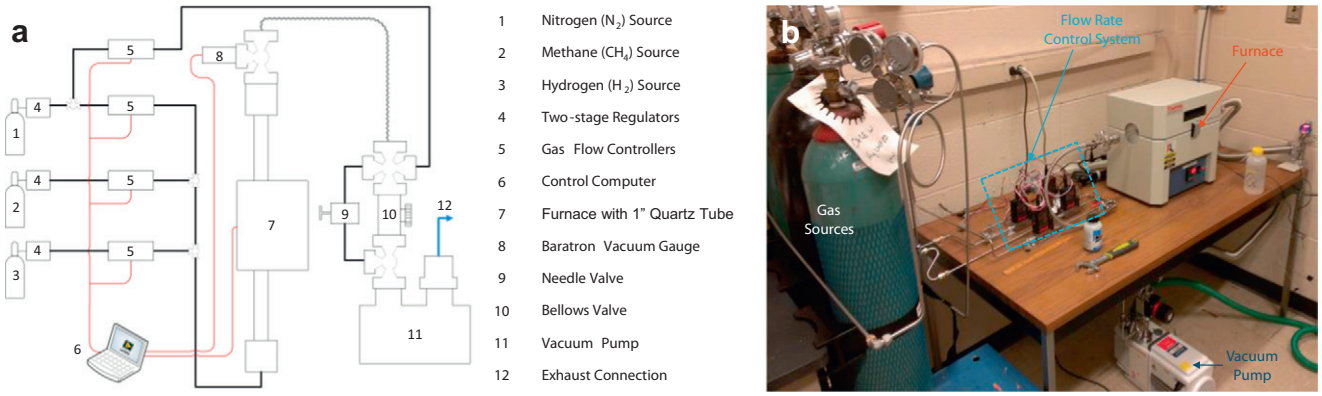

Fig. 1. The home-built CVD synthesis system used for the graphene growth. (a) A detailed illustration of the graphene CVD system design. Major components of the system are identified by numbers. (b) A photograph of the graphene CVD system with components labeled.

2.1. Graphene growth processes

We synthesized graphene on 25 μm-thick Alfa Aesar 99.8% Cu foils [2]. The CVD growth chamber was comprised of a 1-inch diameter quartz tube in a horizontal split-tube furnace. Computer programmed gas flows were obtained by using the mass flow controllers (Alicat Scientific) and the vacuum pressure level was monitored via a capacitive manometer gauge (Fig. 1a). Before synthesis, Cu foils were cut into ~1 cm × ~1 cm squares and chemically cleaned using acetic acid at 35 °C for 15 min, which removed copper oxide on Cu foil surfaces [10]. Then, two pieces of cleaned Cu substrates were introduced to the center position of the quartz tube. A vacuum pump was used to achieve ~5 mTorr base pressure in the tube.

Upon completing the preparation steps, the growth process consists of three major steps: pre-annealing, graphene synthesis, and cooling down (Fig. 2). For the pre-annealing part, a 6 sccm hydrogen (H_2) gas flow was introduced, as the growth tube was heated to 1000 °C. Once the set temperature had been reached, pre-annealing of the Cu substrates was conducted for 60 min, which stabilized the temperature of substrates, further cleaned Cu surfaces [11,12], and generated larger Cu grains by merging small ones. Next, graphene synthesis began by introducing methane (CH_4) gas to the tube as the carbon source. To determine the optimal CH_4 concentration, we conducted variable CH_4 flow rates (10 sccm, 30 sccm, and 50 sccm), along with constant H_2 flow rate (6 sccm), different chamber pressures (1 to 10 Torr) and growth durations (4 to 16 min). Detailed recipes are summarized in Table 1. After the growth step had been finished, the furnace was cooled down. Once temperature reached 200 °C, CH_4 and H_2 flow was stopped and nitrogen (N_2) was introduced into the quartz tube. The Cu foils were then unloaded near room temperature, with synthesized graphene on them.

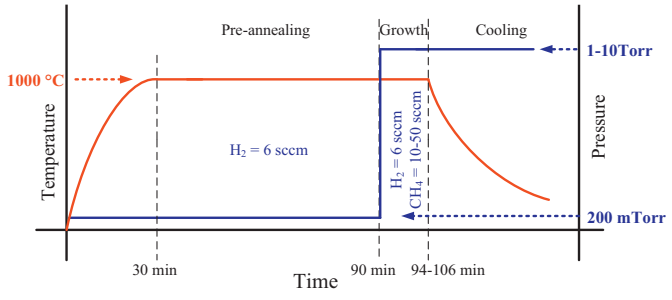

Fig. 2. A standard graphene CVD synthesis recipe (recipes #1-8 in Table 1), illustrated with temperature, duration and gas pressure used for each step. Red lines and blue lines show temperature and gas pressure in the tube during the growth, respectively.

2.2. Characterization of graphene for optimizing growth parameters

Using SEM and Raman spectroscopy, we examined multiple samples of graphene grown by different recipes. Raman spectra were recorded by a customized micro Raman setup. A 532 nm green laser was focused by a 100× optical microscope with a typical spot size on the sample of 1 μm. Before signal acquisition, the monochrometer of the Raman system was calibrated by measuring an undoped silicon TO peak (520 cm^{-1}) for zero backlash. By comparing the images and Raman spectra, an optimized recipe of CVD synthesized graphene was obtained.

Fig. 3 shows examples of measured Raman spectra and SEM images of CVD graphene with different growth conditions. We found pronounced graphene G and 2D peaks from the Raman results. Regardless of graphene growth recipes, in majority of Raman results, full width at half maximum (FWHM) of the 2D peak are narrower than 32 cm^{-1} (Table 2), and the D peak (related to defect density of graphene) is either very small or invisible. These results indicate that the graphene samples synthesized by almost all of our CVD growth recipes are of high quality [13,14].

By using SEM, we have also observed surface morphology of CVD graphene grown by different growth recipes (as shown in Table 1). All SEM images in Fig. 3 were taken by using an FEI Helios NanoLab SEM with an Everhart-Thornley detector (ETD). In these SEM images, bright small clusters, typically ~50 nm, are visible. As the sizes of these clusters are much smaller than the Raman laser spot size (~1 μm), it has been difficult to efficiently characterize these bright dots using Raman spectroscopy when the cluster density is low. To identify these clusters, we intentionally introduced 10 sccm of forming gas (95% N_2, 5% H_2) together with 30 sccm of CH_4 into the growth tube at 1000 °C for 3 h to increase the cluster density. As shown in Fig. 3g, clusters with the density of ~30/μm^2 are formed on Cu substrates, dense enough for Raman measurement. Fig. 3h shows the measured Raman spectrum

Table 1
Summary of graphene growth recipes examined in this study.

Recipe ID	Gas flow rate [sccm]	Chamber pressure [Torr]	Growth time [min]
1	$H_2 = 6$, $CH_4 = 30$	5	16
2	$H_2 = 6$, $CH_4 = 30$	2	16
3	$H_2 = 6$, $CH_4 = 30$	1	16
4	$H_2 = 6$, $CH_4 = 30$	1	10
5	$H_2 = 6$, $CH_4 = 30$	1	5
6	$H_2 = 6$, $CH_4 = 50$	2	16
7	$H_2 = 6$, $CH_4 = 10$	2	16
8	$H_2 = 6$, $CH_4 = 50$	10	4
9	95%N_2 + 5%H_2 = 10, $CH_4 = 30$	5	180