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Correlating nucleation density with heating ramp rates in continuous graphene film formation

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ABSTRACT

Graphene films with different nucleation densities were successfully grown on Cu foils using an atmospheric pressure chemical vapor deposition (APCVD) method. We investigated the effect of heating ramp rate on graphene growth, which is critical to the control of both the domain density and the defects density in further synthesized graphene film. Density of graphene domains was reduced with a decrease in ramp rate; heating Cu foil at a lower rate produced flat and smooth surface with larger Cu grains. These surface roughness and grain size-heating rate association were confirmed by atomic force microscope and electron backscatter diffraction analysis. By comparing micro Raman mappings of the graphene films grown with different ramp rates, we found that the number of layers, defect density, and uniformity of as-grown graphene films were strongly dependent on heating ramp rate. With these observations, we demonstrate the growth mechanism of graphene films as a function of the heating ramp rates.

1. Introduction

Graphene, which is a monolayer of sp^2-bonded carbon atoms, is a two-dimensional (2D) material that has been attracting great interest because of its fascinating structural and electrical properties [1]. The extremely high electron mobility of Graphene and its tunable band gap make it potentially attractive for use in innovative electronic and sensing devices [2–5]. Since the first demonstration of its synthesis by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) [6], a number of alternative synthesis methods have been developed. These include decomposition of SiC surfaces by thermal treatments [7], synthesis using the solution phase [8,9], solvothermal synthesis of graphene [10,11], and chemical vapor deposition (CVD) of graphene on transition metals [12–17]. Of all these approaches, the CVD method is the most effective for device fabrication since it is highly reproducible and yields high-quality films of controllable thickness [18,19]. In particular, graphene films grown on Cu foil by CVD have attracted much interest, because it can produce large area monolayer graphene films due to its low solubility of carbon in Cu, which can be applicable for wafer scale

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Abbreviations: APCVD, atmospheric pressure chemical vapor deposition; R_r, heating ramp rate; SEM, scanning electron microscopy; AFM, atomic force microscopy; rms, root mean square; EBSD, electron back-scattered diffraction
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graphene-based devices and circuits [17,20]. Furthermore, atmospheric pressure CVD (APCVD) is highly suited for synthesis of large-scale graphene films as it is a cost-effective, scalable, quick, and high-throughput method. During CVD, various factors affect the initiation of the graphene nucleation process such as the surface microstructure of the metal catalyst [21], the carbon source used [22], surface oxygen [23], and the reaction parameters used during CVD growth [24–26]. However, a number of other factors involved in CVD growth of graphene films have not yet been studied fully and need to be elucidated so that graphene films with low defects density can be fabricated.

In general, it has been found that the presence of domain boundaries in synthesized graphene films has a detrimental effect on their fundamental electronic properties [27,28]. Therefore, it is recently reported to grow graphene domains on liquid copper [29,30] or resolidified copper in order to decrease the number of domain boundaries, increasing each size of graphene domains and hence decrease the defects density of large-area, monolayer graphene films [31–34]. However, graphene grown on liquid or resolidified copper has some drawbacks such as difficulties in transferring on other substrates and high temperature needed to melt the copper and still challenges [34]. Owing to the fact that initial nucleation of graphene domains takes place more readily at step edges, folds, and other imperfections on the Cu foil used as substrate, the existence of graphene domains as well as their number depends strongly on the topography of the Cu foil surface. It is well-known that the density of graphene domains can be suppressed by increasing growth temperature or annealing time, because the number of step edges, folds, and other defects are reduced at higher growth temperatures or by annealing for longer periods [26,35]. Having lower defects density on the Cu foil surface results in a lower density of nucleation sites and thus fewer graphene domains [36].

In this study, we investigated the effects of heating ramp rate on the growth of graphene films by monitoring the characteristics of graphene domains such as nucleation density during the initial stage of graphene nucleation. To elucidate the role of heating ramp rate on graphene growth, we synthesized graphene domains and films on Cu foil using various ramp rates and measured the densities of graphene domains, the roughness of Cu surface, and the size of Cu grains. Characterization techniques, such as scanning electron microscopy (SEM), atomic force microscopy (AFM), and electron back-scatter diffraction (EBSD) analyses were employed to obtain the correlation of nucleation density with heating ramp rates. In addition, we characterized graphene films grown with different ramp rates using ultraviolet–visible (UV–vis) spectroscopy and micro-Raman spectroscopy.

2. Experiment

The graphene films were synthesized using the APCVD method. The Cu foil used as substrate (25 μm thick, 99.999%, Alfa Aesar) was first cleaned with acetone, isopropyl alcohol, and deionized (DI) water. The foil was then placed in a 1 inch-diameter quartz tube, and the tube put inside a horizontal furnace (Lindberg/Blue M, Thermo Scientific). The system was evacuated for 10 min. Next, the pump was isolated, and the growth chamber brought back to atmospheric pressure by introducing a H_2 and Ar. This process was repeated several times, all at room temperature. The Cu foil was then heated to 1050 °C using one of several selected ramp rates (35 °C/min, 18 °C/min, or 9 °C/min) in the H_2 and Ar atmosphere. For the initial Cu cleaning and annealing, the sample was maintained under the same temperature and atmosphere as the annealing process for another 1 h. Then, the supply of Ar was shut off, and methane was introduced for graphene growth. The flow setup for this stage consisted of 300 sccm of diluted methane (50 ppm in Ar), along with 20 sccm of H_2, flowing into the reaction tube. Process times used were 10 min for identification of initial graphene nucleation and 60 min for film growth. Finally, the samples were rapidly cooled to room temperature (20 °C/s) in a protective atmosphere of Ar and H_2. (see the Supplementary information Fig. S1 for the detailed description of the experiment.) The annealing and growth conditions, and the cooling rate were the same for all samples, in order to minimize variations in the characteristics of synthesized films owing to these factors. We only varied heating ramp rates in each experiment.

Scanning electron microscopy (SEM) images of the synthesized graphene flakes were obtained using a field-emission SEM system (JEOL 7600F) operated at acceleration voltages of 10–20 kV. AFM and EBSD analyses were performed to identify the surface roughness and crystallographic nature of the Cu foil samples, respectively. Raman spectra of the synthesized graphene samples were obtained using a laboratory-made micro-Raman spectroscopy system; the system used the 514.5 nm line of an Ar ion laser as excitation source with a power of ~1 mW. The heating effect of the laser could be neglected at this power level. The laser beam was focused onto the graphene sample using a 50× microscope objective lens (Numerical Aperture = 0.8). The collected scattered light was dispersed using a Shamrock SR 303i spectrometer (1200 grooves/mm) and was detected using a charge-coupled device (CCD) detector.

3. Results and discussion

As mentioned previously, we investigated the effects of heating ramp rate on initial nucleation density of graphene domains during APCVD growth of graphene films on Cu foil. Fig. 1(a–c) shows SEM images of the graphene domains grown on Cu foil using different ramp rates, namely, 35 °C/min, 18 °C/min, and 9 °C/min and transferred on SiO_2/Si substrates; these rates are denoted as R_r-°C/min in the figure. The graphene domains synthesized in the case of R_r-35 (i.e., for a ramp rate of 35 °C/min) were densely distributed on the Cu surface (Fig. 1(a)). However, the R_r-18 condition (i.e., a rate of 18 °C/min) resulted in less densely distributed graphene domains (Fig. 1(b)). Finally, R_r-9 (i.e., 9 °C/min) resulted in graphene domains with a significantly lowered nucleation density (Fig. 1(c)). This tendency was also correspond to the results of graphene domains grown for 30 min with different ramp rates. (see the Supplementary information Fig. S2) On the basis of the above-mentioned results, it could be concluded that a low heating ramp rate (R_r-9) has a similar effect on density of graphene domains as