Hydrogen-Assisted Fast Growth of Large Graphene Grains by Recrystallization of Nanograins

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ABSTRACT: Chemical vapor deposition has been highlighted as a promising tool for facile graphene growth in a large area. However, grain boundaries impose detrimental effects on the mechanical strength or electrical mobility of graphene. Here, we demonstrate that high-pressure hydrogen treatment in the preannealing step plays a key role in fast and large grain growth and leads to the successful synthesis of large grain graphene in 10 s. Large single grains with a maximum size of ∼160 μm grow by recrystallization of nanograins, but ∼1% areal coverage of nanograins remains with 28°–30° misorientation angles. Our findings will provide insights into mass production of high-quality graphene.

1. INTRODUCTION

Chemical vapor deposition (CVD) is the most widespread method for single-layer graphene growth in a large area for electronic or filter applications.1−7 However, CVD-grown graphene typically has grain boundaries that severely deteriorate the electrical, optical, and mechanical properties of graphene.8−12 Thus, the fast-growth method of single-crystalline graphene has been intensively studied for mass production of high-quality graphene.3,4,13,14 One of the growth strategies for single-crystalline graphene is suppressing nucleation sites by regulating carbon feedstock gas or external oxygen supply.3,4,13 However, this process suffers from either formation of randomly oriented multiple seeds or a slow growth rate.

Another approach to improving the grain size and growth rate of graphene is the preannealing treatment of a substrate in a hydrogen atmosphere, in which segregated hydrogen on the surface affects both the substrate itself and the graphene growth.7,14 Hydrogen eliminates the surface oxides or impurities and makes graphene nucleation sites active.15,16 In the graphene growth step, hydrogen makes carbon atoms in graphene stable, elevating the graphene growth rate.17,18 Although, the high growth rate of graphene with the high-pressure preannealing process inevitably accompanies small grains from lots of nucleation sites. Here, we realize the fast growth of single-layer graphene with a hundred micron-scaled grains. For the fast growth of large grains, we initially grow nanograins and prompt their recrystallization by manipulating hydrogen partial pressure. To investigate hydrogen effects on grain size, the graphene grown at different hydrogen pressures is analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy.

2. EXPERIMENTAL METHODS

Graphene was synthesized on 25 μm thick high-purity Cu foil (purity 99.999%, Alfa Aesar) by low-pressure CVD. Before the growth of graphene by CVD, the surface of the Cu foil was treated in a 20% H2PO4 solution and cleaned by deionized water several times. For CVD-grown graphene, the Cu foil was placed inside a quartz tube and heated to 1035 °C for 40 min. During the entire process from heating to growth, hydrogen pressure was fixed to 3 Torr (200 sccm) before the cooling stage. The annealing process of the Cu foil was instantly started after the heating stage and maintained for ∼2 h at 1035 °C under a hydrogen atmosphere. Afterward, a 0.5 Torr (60 Torr) flow rate of methane was injected into the quartz tube for a few seconds as the growth stage at 1035 °C. The growth time of graphene was controlled by measuring the time period from when the gas valve was opened to that when it was closed. The gas flow was turned off during the cooling stage and the Cu foil was finally extracted from the quartz tube. The schematic graphene growth process that enables fast and large grain growth is depicted in Figure S1. Graphene was transferred by conventional polymethyl methacrylate (PMMA) coating technique on the SiO2/Si substrate or TEM grids for characterization. Graphene was coated by PMMA through spin coating for 60 s at 1000 rpm and cured at 200 °C for 10 min. Then, the Cu foil substrate was chemically etched away by a 0.1 M Na2S2O4 solution for over 6 h. The remaining chemicals were rinsed by deionized water at 50 °C 5
times. After PMMA-coated graphene was transferred on the targeted substrate, PMMA was removed by acetone, and 5 h thermal annealing was carried out for eliminating residual PMMA at 350 °C in the quartz tube (H₂ 100 sccm, Ar 500 sccm).

Graphene morphology and coverage according to growth time was analyzed by 1 kV accelerated SEM (Magellan 400, FEI company) on the as-grown Cu foil. The surface chemical state analysis of the Cu foil after hydrogen annealing was conducted by X-ray photoelectron spectroscopy (XPS, Sigma Probe, Thermo VG Probe). TEM dark-field images of graphene were observed by a 120 kV accelerated electron beam in TEM (JEOL-2100F, JEOL). Before TEM observation, the graphene-supporting substrate was heated at 120 °C for 1 h to eliminate surface-bound carbon. Raman spectroscopy (LabRAM HR Evolution Visible_NIR, HORIBA) analysis of graphene on SiO₂/Si was carried out for characterizing the graphene defect structure, and its laser excitation wavelength was 514 nm. Atomic force microscopy (AFM, Dimension XR, Bruker) in non-contact mode was used for characterizing the thickness of the grown graphene after being transferred on the Si substrate.

3. RESULTS AND DISCUSSION

To investigate the effects of hydrogen on the nucleation and growth steps, SEM and TEM imaging are conducted on the graphene grown on the preannealed Cu foil with 0.1 Torr low-pressure hydrogen (LPH) and 3 Torr high-pressure hydrogen (HPH) (Figure 1). Graphene covers ~95% of the area in the HPH condition in 1 s and fully covers the 6 cm × 3 cm foil in 5 s, where the growth rate is ~3.6 cm²/s (Figure S2). On the other hand, graphene has only ~45% coverage and forms islands in the LPH condition in 1 s, showing complete coverage in 20 s with a growth rate of ~0.9 cm²/s (Figure S3). Graphene has continuous film-like morphology even in a half-second in the HPH condition with ~90% coverage (Figure 1a,b). Graphene growth on the catalytic Cu surface could follow the following kinetic model

\[ V_{\text{coverage}} = \frac{d \text{coverage}}{dt} = \alpha (1 - \text{coverage}) \]

where \( \alpha \) and \( (1 - \text{coverage}) \) individually denote the growth rate and fraction of bare Cu, owing to the reduced catalytic area as graphene coverage increases. Thus, the coverage rate is expressed as

\[ \text{coverage} = -e^{-\alpha t} + 1 \]

As a result, growth rate, \( \alpha \), values of 0.141 and 0.994 s⁻¹ are individually attained by fitting the coverage versus time graph in LPH and HPH conditions, showing the fast growth of graphene in HPH compared to that in the LPH condition (Figure 1c). Also, the graphene growth rate evaluated by coverage area (cm²/s) exhibits an ~4 times higher value in the HPH condition than that in the LPH condition (Figure 1d). Graphene growth rates of ~1.8 and ~0.1 cm²/s are obtained in ~1 Torr intermediate-pressure hydrogen (IPH) and pure Ar environments, respectively (Figures S4 and S5). These results clearly indicate that the graphene growth rate increases with hydrogen pressure.

The surface chemical analysis of the Cu foil using XPS shows the narrowing of the Cu 2p peak with FWHM decrease in the hydrogen-annealed foil compared to bare foil and Ar-
annealed foil, which indicates the transition of Cu₂O to Cu by hydrogen treatment (Figure S8). In other words, it is expected that hydrogen annealing increases the number of nucleation sites, leading a fast growth. In addition, hydrogen stored in bulk Cu during preannealing promotes carbon attachment to graphene by lowering its activation energy. Increased growth rate according to hydrogen partial pressure is consistent with the effect of preannealing on the Cu substrate. Dark-field TEM (DF-TEM) mapping and the selected-area electron diffraction (SAED) pattern are acquired from the graphene grown in LPH and HPH conditions for 20 s of both full coverage (Figure 1e–f). Graphene grown in LPH shows ~1 μm sized grains with random orientations, similar to the graphene grown in HPH and Ar conditions (Figures S4 and S5), but the HPH one shows single-crystalline large grains. Generally, nucleation sites increase with the partial pressure of hydrogen in preannealing, so that small-sized grains are expected in the HPH condition compared to the LPH case. However, large grain size is realized in the HPH condition, implicating that the growth dynamics of HPH follows uncommon nucleation and growth phenomenon.

To examine the origin of the unusual graphene growth process at high hydrogen pressure conditions, DF-TEM analysis is conducted for the graphene grown for 1, 5, and...
10 s (Figure 2). Initial graphene has randomly oriented nanograins with sizes in the range of 10−100 μm and a high nucleation density of ~10⁹/cm² (Figure 2a). Single grains start growing in 5 s, and micron-scaled single grains are completely grown in 10 s (Figure 2b,c). Remarkably, most of the remaining nanograins are embedded in large grains and exhibit highly preferred 28°−30° misorientation angles relative to large grains. The number of nanograins decreases with growth time, while the grain size increases to the micron scale (Figure 2d). Consequently, nanograins grow into large single grains except for 1.4% of the area of embedded nanograins (Figure 2e). Figure 2f shows the misorientation angle changes of grains. Initially formed nanograins exhibit random orientations. Misorientation angles near 2°−3 and 28°−30° increase with grain growth, but eventually most of the grains present high-angle grain boundaries (HAGB) with 28°−30° misorientation angles, where grain boundaries have local minimum energies.22,23 These results indicate that most of the nanograins are recrystallized via grain coalescence except for few of 28°−30° misoriented ones.

After complete recrystallization, the size of a large single grain reaches ~160 μm in the 10 s condition. DF-TEM observation clearly indicates the growth of large single grains except for embedded grains (Figure 3).

A detailed recrystallization process is further investigated by observation of nanograins in the 5 s condition (Figure 4). In several positions, locally merged nanograins are envisaged by DF-TEM, where the maximum size is ~1 μm, including small nanograins of ~100 nm in the vicinity of them (Figure 4a). Differently oriented DF mappings clearly show the presence of both as-grown small nanograins and merged ones. In this stage, however, no embedded grains are observed, and thus, the recrystallization process is still in the intermediate step. On the other hand, micron-scaled single grains with embedded nanograins of 28°−30° misorientation angles are observed in other positions (Figure 4b). These single grains are generally over ~1 μm and surrounded by many nanograins. Thus, it is...
considered that recrystallization of nanograins is accomplished in two stages (Figure 4c). At the first stage, nanograins are locally merged by continuous growth, but growth is terminated when the grain sizes reach $\sim 1\ \mu m$. At the same time, directional recrystallization arises in a bunch of nanograins and forms large single grains by continuously taking up surrounding nanograins. Indeed, the embedded grains exhibit under $\sim 1\ \mu m$ grain sizes, indicating inclusion of locally merged grains into large single grains (Figure 4d). In other words, recrystallization stages 1 and 2 are distinguished from the presence or absence of both embedded grains and large single grains. Directional recrystallization would be originated from high grain boundary energy in nanograins for reducing its energy.$^{24}$ Owing to directional recrystallization, randomly distributed nanograins are aligned to a single direction except for $28^\circ - 30^\circ$-misoriented grains.

To unveil the formation mechanism of $28^\circ - 30^\circ$-misoriented embedded grains during recrystallization, DF-TEM mappings on both large single grains and $28^\circ - 30^\circ$-misoriented grains are carried out in the 5 s condition (Figure 5). Typically, it is conceived that embedded grains are generated from the simple merging of as-grown nanograins or new formation during directional recrystallization. As depicted in combined image sets from both large single grains and $28^\circ - 30^\circ$-misoriented grains, misoriented one are already partially embedded in large single grains, despite the progression state of recrystallization (Figure 5a–d). Therefore, it is shown that embedded grains are formed by a simple merging process of misoriented grains with large single grains and are not newly grown from recrystallization. The bulged edge in combined grains supports the simple merging process of two existing large single grains and embedded ones. In other words, stable nanograins with $28^\circ - 30^\circ$ misorientation angles are remained and embedded in large grains, in contrast to the alignment of other misoriented ones. Schematic illustration shows the $28^\circ - 30^\circ$-misoriented...
subgrains formation process during recrystallization (Figure 5e).

To verify the change of graphene quality during the recrystallization process, graphene grown on the HPH-annealed foil is analyzed using Raman spectroscopy and AFM (Figure 6). In the Raman spectrum of graphene, D (~1350 cm⁻¹) and G (~1580 cm⁻¹) peaks originate from the disorder of sp² carbon and the E₂g mode of C–C vibration, respectively. Both D peak intensity and the I_D/I_G value decrease with the growth time, indicating that graphene defects such as grain boundaries are annealed in the recrystallization process (Figure 6a,b). Especially, the I_D/I_G value of 10 s is sharply diminished in the final recrystallization stage, implicating the formation of large single grains. For the graphene composed of nanograins in 1 s, I_D value is unevenly distributed in a 10 μm x 10 μm graphene area, in contrast to a uniform I_D value in large single grains of 10 s (Figure 6c,d).

AFM characterizations of graphene grown for 1 and 10 s are conducted for measuring the thickness of grown graphene (Figure 6e–h). To measure the thickness, AFM topography images are scanned in a 10 μm x 10 μm area of the graphene layer containing a torn region. As a result, graphene layers with a thickness of ~1 nm are measured in both 1 and 10 s grown graphene, implicating the single-layer graphene growth in the HPH condition except for little bilayer region. The discrepancy between graphene thickness of ~0.34 nm with measured ~1 nm could arise owing to the tip–surface interaction or PMMA residue on the graphene surface. In other words, the high quality of single-layer graphene growth is achieved in the HPH condition.

4. CONCLUSIONS

In this work, we demonstrate the fast growth of high-quality graphene with large single grains via recrystallization of nanograins. High-pressurized hydrogen treatment of the Cu foil is a key factor for the recrystallization of nanograins. However, relatively stable nanograins with 28–30° misorientation angles are embedded in large grains. Our results will be helpful in single-crystal graphene growth, which could be applied to graphene liquid cells as an impermeable membrane to gases or liquids.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02701.

Schematic graph for growth conditions (Figure S1); oxidation test of graphene grown Cu foils (Figure S2); SEM images of graphene in LPH conditions (Figure S3); SEM and TEM images of graphene in IPH conditions (Figure S4); SEM and TEM images for graphene on Ar-annealed foils (Figure S5); graphene growth in the 760 Torr condition (Figure S6); Bilayer TEM characterizations (Figure S7); XPS analysis of annealed Cu foils (Figure S8); XRD analysis of annealed Cu foils (Figure S9); DF-TEM analysis of 1 s specimen (Figure S10); DF-TEM images in HPH conditions (Figure S11); tables indicating grain sizes of HPHs according to the growth time (Figure S12); and two-dimensional Raman mappings of the I_G of HPHs (Figure S13) (PDF)

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Notes
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