

Low Density Growth of Graphene by Air Introduction in Atmospheric Pressure Chemical Vapor Deposition

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Chemical vapor deposition (CVD) is a promising method to produce large-size single-crystal graphene, and further increase in domain size is desirable for electro/optic applications. Here we studied the effect of low amount of air introduction by intentional leak on graphene growth in atmospheric pressure CVD. The air introduction at the heating process resulted in roughening of Cu surface induced by oxygen, while air introduction at the annealing under H₂ ambient drastically decreased graphene density due to reduction of active sites for graphene nucleation both by surface oxidation and enlargement of Cu domain. Although air introduction only at the growth stage was ineffective for graphene nucleation, air introduction for both annealing and growth provided great enhancement of domain growth without increasing the density of graphene, which is an optimized condition to obtain a large single-crystal. This controlled introduction of air in atmospheric pressure CVD provided ~ 2.5 mm hexagonal single layer graphene with high quality. [DOI: 10.1380/ejssnt.2015.404]

Keywords: Carbon; Copper; Nucleation; Growth; Graphene; Air

I. INTRODUCTION

High quality graphene provided by mechanical exfoliation from bulk graphite [1-5] has demonstrated attractive fundamental properties such as extraordinary carrier mobility approaching $200,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ [1-5], universal 2.3% optical absorption from mid-infrared to UV light [6], and high Young's modulus of 1 TPa [7]. Regardless of these excellent works, flake size and layer number of graphene formed by the exfoliation method are neither uniform nor controllable, limiting the practical use. In contrast, chemical vapor deposition (CVD) can produce large-area and uniform graphene on catalytic metal surfaces [8, 9], and CVD graphene growth on copper (Cu) shows preferential single layer formation [10] which is suitable for mass production. However, the CVD graphene is generally polycrystalline [11, 12], and its domain boundaries degrade electronic properties such as carrier mobility. Thus, it is desirable for graphene applications [13-18] to grow large single-crystal graphene by improving CVD growth conditions.

Several effective methods to enlarge single-crystal size of graphene/Cu in CVD growth on Cu has been reported such as prolonged annealing [19], electrochemical polishing [20], high pressure annealing [21,22], and suppression of evaporation loss of Cu by wrapping the foil [23]. With these methods, millimeter size graphene domain was achieved. More recently, oxygen was found to play an important role in suppressing graphene nucleation [24,25], and centimeter size graphene was successfully obtained

through the oxygen passivation [25]. Here, we report that a low amount of air introduction during atmospheric pressure CVD processes suppresses graphene nucleation similar to the oxygen passivation. It is found that the air introduction highly affected morphology of Cu surface. The air introduction at each stage of heating, annealing and growth was in detail investigated to clarify the role of the air introduction. By the optimized CVD condition we achieved to obtain millimeter-size hexagonal graphenes. It is noted that our technique neither require any vacuum pump, high quality Cu foils, nor special equipment for air introduction, which is practical for mass production of large single crystal graphenes at a low cost.

II. EXPERIMENTAL

Commercially available Cu foils (Nilaco No. 113321, 100- μm -thick and 99.96% in purity) were electropolished by a custom-built electrochemistry cell. Two Cu foils with the sizes of $\sim 3.5 \text{ cm} \times 10 \text{ cm}$ were placed into a water solution of 500 mL of 1 M KOH in a glass beaker, and were used as anode and cathode. A DC voltage of 4.5 V was applied for 5 min during the polishing process. The Cu foil on the anode was cut into a piece of $\sim 3.5 \text{ cm} \times 2.5 \text{ cm}$ and rinsed with 500 mL deionized (DI) water (2 $\times$), further washed with 50 mL methanol (2 $\times$), and dried by blowing air, and was then introduced in the CVD chamber to grow graphene.

Graphenes were prepared on electropolished Cu foils in lateral quartz-tube CVD equipment (Fig. 1(a)) under nearly ambient pressure (standard atmospheric pressure (P_{atm}) plus $\sim 0.023 \text{ MPa}$). This nearly ambient pres-

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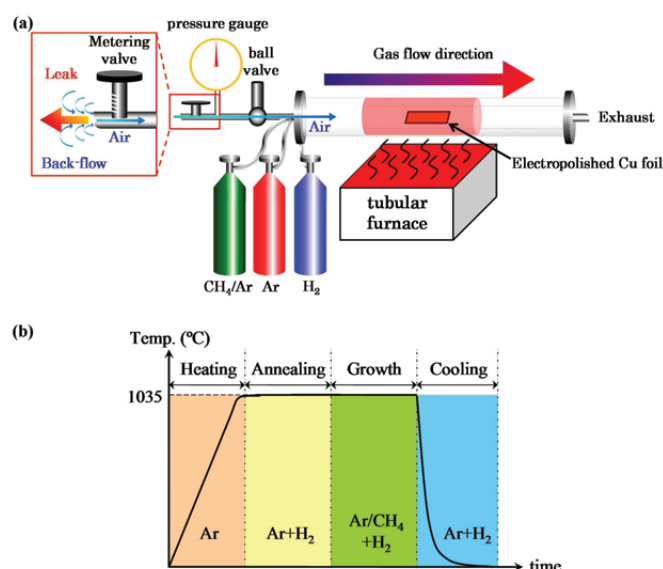


FIG. 1. (a) A schematic illustration of CVD setup and air introduction through back-flow of leak (red rectangular) (b) A schematic illustration of the CVD growth process. CVD process is divided for 4 parts which are heating, annealing, growth, and cooling.

sure was achieved by suppressing the amount of exhaust gasses. Prior to graphene growth, an electropolished Cu foil was heated to 1035°C under Ar flow (1000 standard cubic centimeter per minute: (sccm)) for ~ 45 min, and then annealed under Ar (500 sccm) and H_2 (100 sccm) flows for desirable time, which allows to form nucleation seeds of a large sized graphene [24]. After reducing the H_2 flow rate to be 9 sccm, the graphene growth was initiated by flowing 10 ppm of CH_4 diluted in Ar (500 sccm). Subsequently, the Cu foil was rapidly cooled from 1035°C down to room temperature within less than 30 min under Ar (1000 sccm) and H_2 (9 sccm) flows. The whole CVD process is schematically summarized in Fig. 1(b), and is divided by 4 stages, heating, annealing, growth, and cooling.

Air introduction was performed by intentional leak through a ball valve (BV) and a normally-open metering valve (MV), as schematically shown in Fig. 1(a). When we open the BV, the gasses are leaked through the MV since the pressure of the CVD chamber is higher than atmospheric pressure. At the same time, there must be unavoidable very low amount back-flow of air into the chamber. To confirm the back-flow of air by leak, we monitored the oxygen concentration under Ar ambient by a zirconia oxygen sensor (Toray Engineering LC 750 L). As a result, oxygen concentration increased ~ 1.5 ppm via the leak with closing MV and opening BV (low leak), while oxygen concentration showed lower than 0.1 ppm without leak, proving the existence of low amount of air introduction by the back flow. The amount of air introduction can be varied by adjusting the MV. When the MV has been closed (low leak) and opened for 10° (high leak), approximately 0.02 and 0.04 cm^3 in volume of oxygen (in 1000 sccm Ar flow) have been introduced during the leak process, respectively. In addition, flow rates of

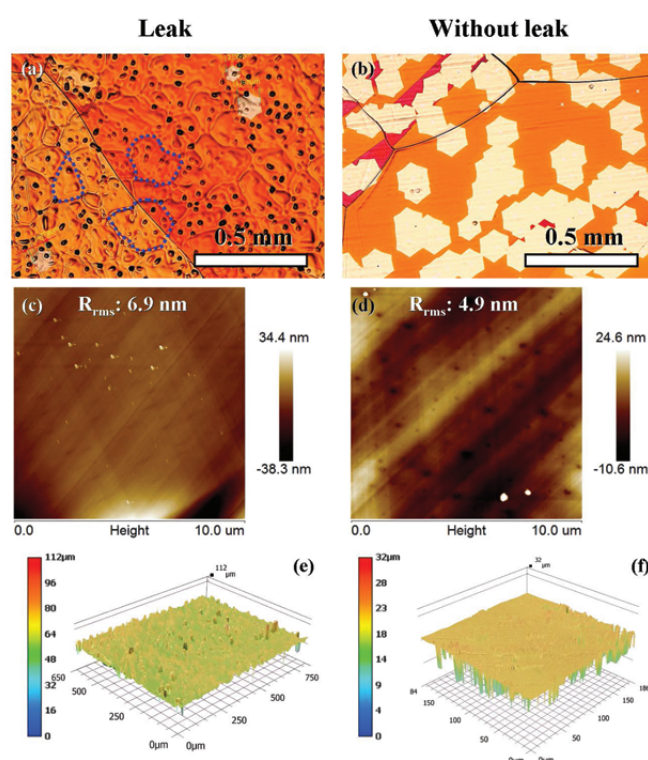


FIG. 2. Effect of leak on graphene growth and surface morphology. Optical microscope images of visualized graphene on Cu which are grown with (a) and without leak (b). Typical AFM images of Cu surface after CVD with (c) and without leak (d). 3D optical images showing large scale morphology of Cu surface after CVD with (e) and without leak (f).

leak which can be used as a parameter for adjusting the amount of air were estimated by monitoring the decay of pressure with time after filling Ar gas and closing the BV.

The graphene on Cu was heated to around 200°C for 2 min in air, which oxidizes only exposed Cu surface, leading large contrast between graphene and Cu in optical microscope image (Keyence Digital Microscope VHX-5000). Detailed surface morphology was observed using an atomic force microscope (AFM; Bruker Multi-Mode 8) in a ScanAsyst[®] mode. X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI5000 Versa Probe II) and Auger electron spectroscopy (AES, ULVAC-PHI PHI700 Xi) were used for surface elemental analysis. The graphenes were wet-transferred from the Cu foils onto the SiO_2/Si substrates with a spin-coated poly (methyl methacrylate) (PMMA) film as a mechanical support [9,26]. Raman spectra and mapping images of the transferred graphene were obtained to characterize the quality of graphene by a commercial Raman microscope (Renishaw InVia) using a 532 nm excitation laser.

III. RESULTS AND DISCUSSIONS

Figures 2(a) and 2(b) show optical microscope images of visualized CVD graphenes on Cu with and without leak, respectively. The leak was conducted during all

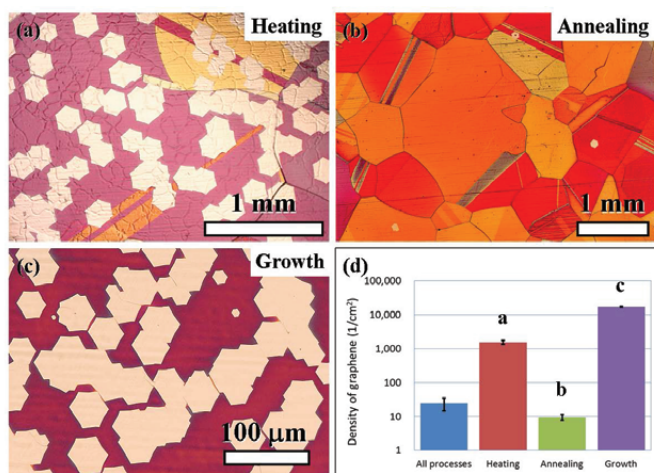


FIG. 3. Effect of leak term on graphene growth. Optical microscope images of visualized graphene on Cu after CVD with leak during heating (a), annealing (b), and growth (c). (d) Comparison of term of air introduction for graphene density.

CVD processes (heating, annealing, growth, and cooling Fig. 1(b)). Hexagonal graphenes showing white contrast in optical images are observed in Figs. 2(a) and (b). The CVD processes with leak produce apparently lower density of graphene than those without leak. The thus drastic change empirically indicates suppression of graphene nucleation by the air introduction. On the other hand, island-like shapes (guided by dotted lines) and black dots are observed in Fig. 2(a) while smooth surface is formed in Fig. 2(b).

Figures 2(c) and 2(d) show typical AFM images of Cu surface after CVD growth with and without leak, respectively. Figures 2(e) and 2(f) show typical 3D optical images showing large scale morphology of Cu surface after CVD growth with and without leak, respectively. The root mean squared roughness (R_{rms}) measured for Fig. 2(c) and Fig. 2(d) shows 6.9 and 4.9 nm, respectively. The values are almost similar in this short range ($< 10 \mu\text{m}$), but are much smoother than that of the electropolished Cu (R_{rms} : 93.3 nm), presumably by virtue of annealing in Ar/H₂ [9]. On the other hand, many protrusions (more than $10 \mu\text{m}$ in height) corresponding to the black dots in Fig. 2(a) were observed only on the Cu surface with leak in the 3D optical image (Fig. 2(e)), indicating that the leak affected Cu morphology on a large scale ($> 100 \mu\text{m}$).

To understand the role of leak, we conducted the leak only at a specified process (heating, annealing or growth) during CVD. Figures 3(a-c) show optical microscope images of CVD graphene with leak only at heating, annealing, and growth, respectively. Figure 3(d) summarizes the graphene density in each figure. Since the leak process at the annealing process only showed low graphene density with similar magnitude of leak at all processes, low amount air introduction at annealing is an effective process for suppressing graphene nucleation.

To clarify the reason of the lowered graphene density by air introduction at annealing, we characterized the surface of annealed Cu foils (45 min at 1035°C) before growth.

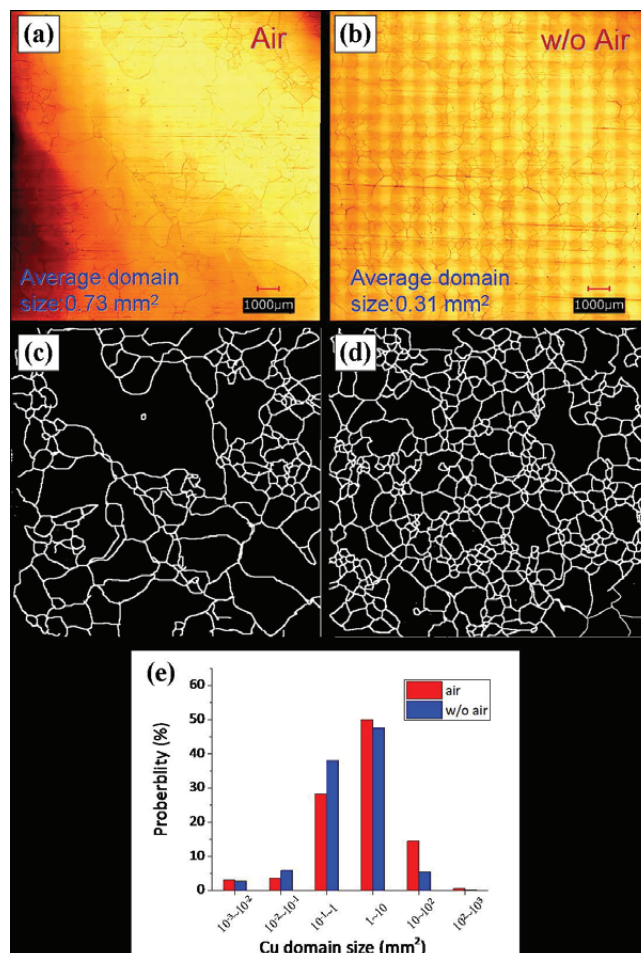


FIG. 4. Optical images of annealed Cu surface with (a) and without (b) air introduction. (c,d) Binarized images converted from (a) and (b) to emphasize domain boundaries of Cu. (e) Histogram of Cu domain size extracted from (c) and (d).

TABLE I. Elemental composition of annealed Cu surface with (air) and without air (w/o air). O/Cu is relative atomic ratio of oxygen for Cu.

	C1s (%)	O1s (%)	Cu2p _{3/2} (%)	O/Cu
air	22.6±0.4	27.8±0.7	49.5±0.6	0.56±0.02
w/o air	19.8±0.3	24.4±0.5	55.7±0.7	0.44±0.01

Figures 4(a) and 4(b) show optical images of Cu surface after annealing with and without leak. Cu crystal domains was observed for both samples (Figs. 4(a) and 4(b)). Figures 4(c) and 4(d) show binarized images of Figs. 4(a) and 4(b). Figure 4(e) shows the size distribution of the Cu domains extracted from the corresponding optical microscope images. The probability of large Cu domain ($> 1\text{mm}^2$) apparently increased by air introduction. In addition, average size of Cu domain also increased by air introduction. Since domain boundary is an active site for graphene nucleation [27], the enlargement of Cu domain by air would be attributed to the lowered graphene density.

The elemental composition of annealed Cu surface was

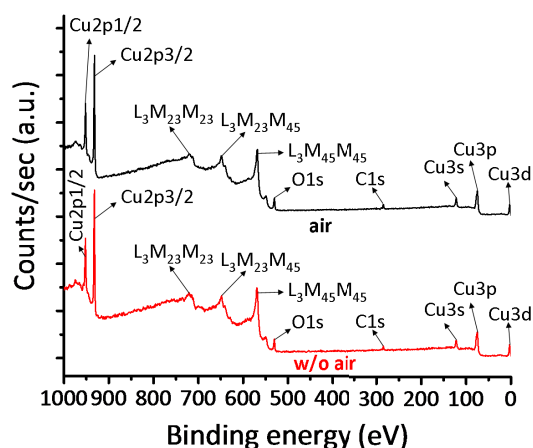


FIG. 5. Representative XPS survey spectra of annealed Cu foils with (black) and without air (red) using 25 W, Al K α (1486.6 eV) radiation.

further examined by XPS. Since Cu surface is oxidized and the chemical state gradually changes with time under ambient air [28], we immediately transferred the annealed Cu foils from CVD to XPS chamber with the same time span (< 10 min). Figure 5 shows representative XPS survey spectra of the annealed Cu foils with and without air introduction. Core-level lines (Cu2p $_{1/2}$, Cu2p $_{3/2}$, Cu3s, Cu3p, Cu3d) and Auger peaks (LMM) of Cu are present. Oxygen (O1s) at 530.5 eV and carbon (C1s) at 285 eV corresponded to oxidation of Cu and adventitious contamination from air on the surface. Table I shows elemental composition of annealed Cu surface with (air) and without air (w/o air) extracted from C1s, O1s, and Cu2p $_{3/2}$ peaks in XPS spectra. The atomic ratio of oxygen of the annealed Cu with air is higher than that without air, which is clearer in O/Cu relative atomic ratios. This indicates that air introduction at annealing oxidized Cu surface. The surface oxidation by air at annealing would passivate active sites for graphene, resulting in suppressing graphene nucleation, which is similar to passivation by oxygen reported in Ref. 25.

On the other hand, a rough Cu surface such like in Fig. 2(a) is only observed after CVD with leak at heating (Fig. 3(a)). This result empirically showed that the air introduction at heating causes roughening of Cu surface which is not desirable for graphene growth.

To investigate the roughening of Cu, we examined the protrusion and flat surface in Fig. 2(a) by AES. As a result, copper, carbon and oxygen signals were detected but no significant difference between the protrusion and the flat region. This result indicates that the surface roughening was not caused by impurities such from the Cu substrate or the quartz tube in CVD furnace but from the main components of the air such as nitrogen, H $_2$ O, and oxygen. Although we cannot exclude intermediate chemical reaction during CVD by nitrogen and H $_2$ O in air, no trace of nitrogen after CVD indicates that surface morphology was affected by oxidation process [24, 29, 30] by H $_2$ O and oxygen in air. Therefore, surface roughening in the present study would be caused by oxidation because

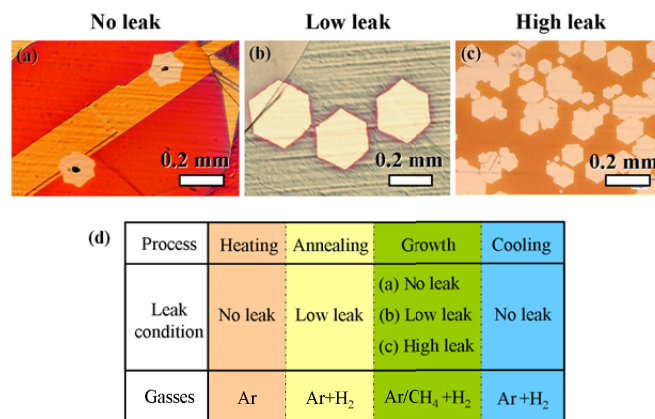


FIG. 6. Comparison of amount of air during the growth stage. Optical images of visualized graphene with different leak conditions during growth stage: (a) no leak; (b) low leak; (c) high leak. (d) Schematic summary of CVD conditions for (a), (b) and (c).

of the absence of reduction gas like at the H $_2$ heating.

To further investigate the effect of air on growth stage, we prepared three different conditions of no, low, and high leaks by closing BV, MV, and opening MV for 10°, respectively. Figures 6(a-c) show graphenes grown for 40 min with no, low, and high leak conditions on Cu that are annealed for 45 min with low leak. Figure 6(d) shows the summary of the process for Figs. 6(a-c). The average diameter and density of graphene domains are measured from optical images and summarized in Table II. The low leak (Fig. 6(b)) leads to twice larger graphene growth than that of no (Fig. 6(a)) and high leak conditions (Fig. 6(c)), even in the same growth time. This acceleration of graphene growth in Fig. 6(c) would be due to growth kinetics change from edge-attachment-limited to diffusion-limited by oxygen, as reported in Ref. 25. On the other hand, high leak (0.20 ± 0.01 sccm) led to dense growth of graphene in Fig. 6(c). This result indicates only very low amount of air introduction (0.14 ± 0.01 sccm) can achieve high growth rate and low density of graphene. The reason for the dense growth in Fig. 6(c) might be that nanoscale dusts in air were introduced by opening MV valve.

Since annealing and growth with low leak resulted in large graphene domain sizes with low density, this condition is used hereafter to obtain large size graphene. Figure 7(a) shows dependence of graphene density on annealing time with low leak during the annealing and growth processes. Graphene nucleation is drastically suppressed by annealing up to 60 min, and becomes lower than 10 cm^{-2} with gradual decay after 180 min annealing. Figure 7(b) shows an optical microscope image of the graphene with long time annealing (4 h) and growth (3.5 h). Approximately 2.5 mm graphenes were observed in a magnified image (Fig. 7(c)), and the hexagonal shape of domains indicates a single crystal [24, 25].

Figures 8 show Raman spectroscopy analysis for millimeter-scale graphene transferred onto a SiO $_2$ /Si substrate. Figure 8(a) shows an optical microscope image of a single hexagonal graphene domain. Figure 8(b) shows

TABLE II. Summary of graphene growth with different leak conditions during growth stage.

Sample	Valve conditions	Leak rate (sccm)	Average diameter of graphene (μm)	Density ($1/\text{cm}^2$)
No leak	BV close	0	81 ± 22	14 ± 7
Low leak	MV close	0.14 ± 0.01	179 ± 15	27 ± 8
High leak	10° open (MV)	0.20 ± 0.01	75 ± 3	14100 ± 500

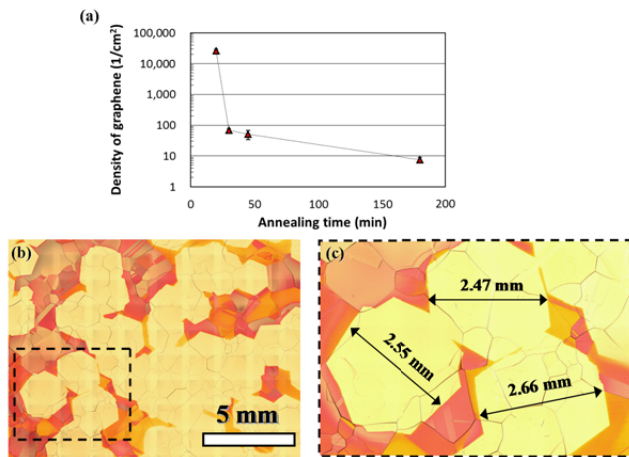


FIG. 7. Large scale graphene growth. (a) Dependence of graphene density on annealing time with leak. (b) Optical image of visualized large-size graphene grown by 4 h annealing and 3.5 h growth. (c) Enlarged view of (b).

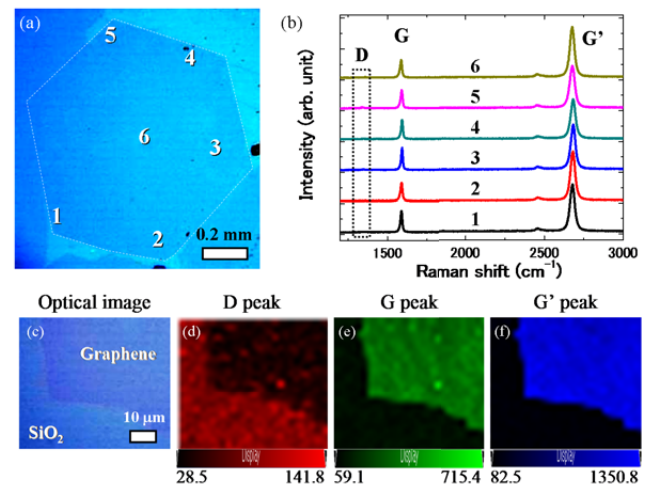
TABLE III. Average peak properties of Raman spectra in Fig. 6(b). Each peak was analyzed by fitting with a Lorentzian curve. Width means full width at half maximum.

G center (cm^{-1})	G width (cm^{-1})	G' center (cm^{-1})	G' width (cm^{-1})	G/D	G'/G
1588.9 ± 0.4	12.3 ± 0.3	2679.1 ± 0.5	31.2 ± 0.2	63 ± 5	2.4 ± 0.1

Raman spectra taken at position 1-6 in Fig. 8(a). Each spectra show similar features of D, G, and G' peaks, indicating uniform quality and layer numbers of graphene in a large domain. Average peak properties of the six spectra are summarized in Table III. Narrow G' peak width ($< 40 \text{ cm}^{-1}$), low G' peak center position ($< 2700 \text{ cm}^{-1}$), and high G'/G peak intensity ratio (> 2) indicates single layer [31]. High G/D peak intensity ratio indicates excellent quality of graphene [31, 32]. Figures 8(c-f) show a magnified optical microscope image, D, G, and G' peak maps around the corner of the graphene domain, respectively, showing high uniformity both in quality and in number of layer on a short scale.

IV. CONCLUSIONS

Effect of low amount of air introduction in atmospheric pressure CVD on graphene growth was studied. Air introduction for all the CVD processes leads to low graphene

FIG. 8. Raman spectroscopic analysis for large-size transferred graphene on SiO₂/Si. (a) Optical microscope image of a single hexagonal graphene domain. The domain shape is guided by white dotted lines. (b) Stacked Raman spectra taken at 6 different points in a graphene domain. Numbers (1-6) are corresponding to the position in (a). (c) Magnified optical microscope image around the corner of the graphene domain in (a). (d-f) Raman mappings of (c) for D, G, and G' peak show uniformity in quality and layer number of graphene. The mapping images are shown in color scale, and high intensity correspond to red, green, and blue for D, G, and G' as shown in color bars at the bottom of each image. Numerical values at the lower left and right of the mapping images correspond to the lowest and highest peak intensity in each mapping image, respectively.

nucleation, but rough surface is formed by oxidation of Cu. By limiting the air introduction at a specified process (heating, annealing or growth), it was revealed that the roughening was caused by excess oxidation of Cu at the heating, and the graphene nucleation was effectively suppressed due to the reduction of active sites for graphene nucleation both by surface oxidation and enlargement of Cu domain. Although air introduction only at the growth stage was ineffective for graphene nucleation, air introduction for both annealing and growth provided enhancement of domain growth without increasing the density of graphene. Finally, $\sim 2.5 \text{ mm}$ hexagonal graphenes were successfully obtained by low amount air introduction in atmospheric pressure CVD. On the other hand, the fact that back-flow of air readily changes graphene growth claims the importance of careful control of air in a CVD chamber. A careful control of air in CVD chamber will minimize day to day variation of the graphene growth and will be more important for large-size graphene growth

beyond millimeter scale. To our knowledge, it is the first report of air introduction for suppressing nucleation in atmospheric pressure CVD on a Cu foil. It is also noted that this low amount air introduction is effective and practical for the scalable production of high quality large-size single-crystal graphene at low cost.

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