Ten-Second Epitaxy of Cu on Repeatedly Used Sapphire for Practical Production of High-Quality Graphene

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Supporting Information

ABSTRACT: Epitaxial copper (Cu) films yield graphene with superior quality but at high cost. We report 1−3 μm thick epitaxial Cu films prepared on c plane sapphire substrates in 10−30 s, which is much faster than that of the typical sputtering method. Such rapid deposition is realized by vapor deposition using a Cu source heated to 1700−1800 °C, which is much higher than its melting point of 1085 °C. Continuous graphene films, either bilayer or single-layer, are obtained on the epitaxial Cu by chemical vapor deposition and transferred to carrier substrates. The sapphire substrates can be reused five to six times maintaining the quality of the epitaxial Cu films and graphene. The mechanisms and requirements are discussed for such quick epitaxy of Cu on reused sapphire, which will enable high-quality graphene production at lower cost.

INTRODUCTION

Graphene has been applied in various electric devices because of its attractive properties such as high carrier mobility, optical transparency, and flexibility.1,2 The large-area synthesis of graphene on polycrystalline copper (Cu) foil has been achieved by the chemical vapor deposition (CVD) method.3 Also, the roll-to-roll transfer process of graphene from Cu foils to insulating plastic substrates, aiming for industrialization, has been reported.4,5 Although CVD provides continuous graphene films in arbitrary sizes, polycrystalline films have numerous domain boundaries and a random orientation,6-8 which will deteriorate their desirable properties.9 Many works on topics including the electropolishing and annealing10 of polycrystalline Cu foils, adjusting the pressure of the carbon source and electrochemical transfer of graphene three times.26 Their method is excellent for avoiding the time-consuming sputtering process taking 1 h for a 300 nm thick Ir layer in the later cycles but graphene transfer with catalyst-etching is still more popular due to the suppressed damage to graphene. Hence, much faster fabrication of epitaxial Cu films on reusable c plane sapphire substrate is highly desirable for the low-cost production and wide use of epitaxial graphene films.

Here, we report the quick preparation of 1−3 μm thick epitaxial Cu films on c plane sapphire substrates within 10−30 s using the rapid vapor deposition (RVD) method that we previously developed for Si films.27 The deposition rate is ~100 nm/s, which is 2−3 orders of magnitude larger than that of sputtering. Such rapid deposition is realized by heating the Cu source to 1700−1800 °C, which is much higher than its melting point of 1085 °C, to elevate its vapor pressure. We also report continuous graphene films, which are either single-layer or bilayer, on the deposited Cu films by CVD and the repeated use of the sapphire substrates for such epitaxial Cu and graphene film production.

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RESULTS AND DISCUSSION

The deposition of epitaxial films is normally performed under ultrahigh vacuum, to avoid the disturbance of crystal growth by contamination gases, with a small deposition rate to allow the deposited atoms to diffuse sufficiently over the substrate/film surface. Our RVD method is based on the opposite concept; we deposit Cu at a very high rate in the presence of “diluted” contaminant gases with Cu vapor avoiding the need for the ultrahigh vacuum, and heat the substrate/film to promote the surface diffusion of Cu atoms rapidly depositing on the substrate/film. The vapor pressure of Cu, \( p \), increases with the source temperature \( T \) and reaches \( p = 432 \text{ Pa at } T = 2000 \text{ K (1727 °C)} \), as shown in the Supporting Information, Figure S1.

From the kinetic theory of gases, the collisional frequency \( F \) of Cu to the substrate/film surface is expressed as

\[
F = \frac{1}{4} \bar{v} C = \frac{1}{4} \sqrt{\frac{8kT}{\pi m}} p = \frac{1}{4} \sqrt{\frac{8RT}{\pi M}} p
\]

where \( \bar{v} \), \( C \), and \( m \) are the average velocity, concentration, and mass of the Cu vapor atom, respectively, \( M \) is the molar mass of Cu, \( k \) is the Boltzmann constant, and \( R \) is the gas constant. When Cu has a sticking probability of \( \eta \), the Cu deposition rate \( r \) is expressed as

\[
r = \frac{\eta FM}{\rho}
\]

where \( \rho \) is the mass density of the solid Cu. The maximum available Cu deposition rate \( r_{\text{max}} \) is calculated using these two equations and \( \eta = 1 \), and is plotted on the same graph as the the vapor pressure (Figure S1). Equation 2 gives the value \( r_{\text{max}} = 38 \mu \text{m/s for } T = 2000 \text{ K (1727 °C)} \). The actual deposition rate becomes smaller than this value due to the dilution of the Cu vapor with increasing distance from the Cu source, which is roughly 1/400 for a hemispherical Cu droplet with 2 mm radius and a source—substrate distance of 40 mm. Thus, a deposition rate of \( r = 0.1 \mu \text{m/s} \) is expected for the source temperature of \( T = 2000 \text{ K (1727 °C)} \).

The high vapor pressure of Cu from the hot Cu source is beneficial not only for an enhanced deposition rate but also for the loose requirement of base pressure. If the deposition rate is enhanced by 100 times or more, Cu atoms hit the substrate/film surface 100 times or more frequently than that of the normal deposition case, diluting the effect of the contamination gases. Actually, the Cu films grow epitaxially, as explained later, with a moderate vacuum level; the base pressure and the pressure during RVD are \( 1 \times 10^{-4} \text{ and } 1 \times 10^{-3} \text{ Pa, respectively} \). However, to achieve epitaxial growth, the surface diffusion of Cu atoms on the substrate/film needs to be enhanced by elevating the substrate temperature. The Cu films as-deposited by RVD on the \( c \) plane sapphire substrates were analyzed by X-ray diffraction (XRD) using a Cu Kα line (Figure S2). The \( Cu(200) \) peak is evident in addition to the intense epitaxial \( Cu(111) \) peak in the Cu film deposited at 200 °C whereas the \( Cu(200) \) peak is absent for the Cu films deposited at 300 and 400 °C. Therefore, we fixed the substrate temperature at 400 °C hereafter.

Figure 1. As-deposited Cu films by RVD on SiO\(_2\)/Si (a−c) and \( c \) plane sapphire (d−f); substrates and the films after annealing (g−i and j−l). The Cu films (~3 μm in thickness) were deposited on substrates by RVD at 400 °C for 30 s and then annealed under 100 vol % H\(_2\) at 1050 °C and 760 Torr for 30 min. (a, a′, d, d′, g, j) Optical images, (b, e, h, k) top-view SEM images, (c, f) side-view SEM images, and (i, l) cross-sectional SEM images. (a, d, j) Photos were taken perpendicular to the Cu surface and the camera lens is clearly visible in the images. (a′, d′) Photos taken with a tilt angle of the Cu films prepared under the same conditions as (a, d), respectively, in different batches.
Next, we compared the structures of the Cu films deposited by RVD on LOBAL sapphire and the SiO2/Si substrate at 400 °C. The Cu film deposited on the SiO2/Si substrate displayed a shiny surface in its optical image (Figure 1a), in which the reflected image of the camera lens is visible. However, the Cu film showed a cloudy surface when observed at a tilt angle (Figure 1d). Cu formed a continuous film with grains of around 10–30 μm visible in the top-view scanning electron microscope (SEM) image (Figure 1b). The Cu film deposited in 30 s by RVD had a thickness as large as 3 μm, and had a flat surface with grain boundaries (indicated by a white arrow) visible from the side-view SEM image (Figure 1c). On the other hand, the Cu film deposited on the sapphire substrate displayed a much shinier surface than that of SiO2/Si in its optical image (Figure 1d), even at a tilt angle (Figure 1d'), and a much flatter surface without any grain boundaries, as shown by SEM (Figure 1e,f).

Then we annealed both substrates under pure H2 at 1050 °C for 30 min. The Cu film on the SiO2/Si substrate became discontinuous, showing the color of both the substrate and Cu film (Figure 1g). The Cu film dewetted and formed hemispherical particles (Figure 1h,i), accompanying a mass decrease of 86 μg/cm2 (3.4% of the original mass of the Cu film, calculated from the mass change of the sample before and after annealing), due to sublimation of Cu during annealing. The Cu films on the sapphire substrate retained a continuous and flat film (Figure 1j–l), accompanying much less Cu sublimation of 28 μg/cm2 (0.84%). The different mass change can be explained by the Kelvin effect; the Cu particles have a curved surface and a higher vapor pressure, thus more Cu evaporated from the Cu particles on SiO2/Si than the flat Cu film on sapphire.

The as-deposited Cu films on both substrates were analyzed by XRD using a Cu KR line (Figure 2). The Cu on SiO2/Si was face-centered cubic-Cu (fcc-Cu) and showed a preferred orientation of (111) with a minor peak of (200) in the out-of-plane measurement (Figure 2a), whereas it showed only a weak (220) peak in the in-plane measurement (Figure 2b). The Cu film showed signals without any symmetry of rotation for the (220) diffraction in the phi-scan measurement (Figure 2c). These results show that Cu on SiO2/Si is polycrystalline fcc-Cu. On the other hand, the Cu on LOBAL sapphire showed an intense peak of (111) in the out-of-plane measurement (Figure 2d) and an intense (220) peak in the in-plane measurement (Figure 2e). Note that the (111) and (220) planes are perpendicular to each other. The Cu film on the sapphire substrate showed six-fold symmetry for the (220) diffraction in the phi-scan measurement (Figure 2f). These results show that fcc-Cu forms epitaxially on sapphire. The six-fold symmetry instead of three-fold symmetry shows the twinned structure of the epitaxial Cu.38 There are some minor peaks in the XRD patterns, all of which can be assigned to the fcc-Cu (111) peak of the Cu Kβ line or the peaks from sapphire and Cu2O. Although the Cu source was heated to a very high temperature of 1700–1800 °C, no other elements such as W (evaporation boat) were detected in the Cu films by SEM-energy dispersive X-ray spectroscopy (EDS) other than Cu and C- and O-contaminations (Figure S3). The full width at half-maximum (FWHM) of the Cu(111) peak in the out-of-plane measurement was 0.26 and 0.19° for the Cu film on SiO2/Si (Figure 2a) and sapphire (Figure 2d), respectively. The FWHM value of 0.19° of this work is significantly smaller than the value of 0.25° reported by Lee et al.57 for the 800 nm thick epitaxial Cu film deposited slowly at 0.1 nm/s on sapphire at 150 °C by radio-frequency sputtering with a base pressure of <1 × 10−5 Pa. The FWHM value was not found in any other reports on epitaxial Cu catalysts on sapphire.13–22,24 The small FWHM value shows the good quality of our epitaxial Cu films deposited by RVD quickly at ~100 nm/s, possibly due to the absence of plasma contaminants (Figure S3).
nucleation for the successive 4–19 min. At the initial stage of 1 + 4 min, 10–20 μm sized graphene islands formed (Figure 4a,b). The typical Raman spectrum of the graphene islands showed a 2D/G peak intensity ratio of $I_{2D}/I_G \approx 1$, confirming that the graphene islands were mostly in bilayer form, and a rather large D/G peak intensity ratio of $I_D/I_G = 0.33$, showing some effect of the island edges (Figures 4e and S4). The Raman spectra showed similar patterns at most of the other points (Figure S5a), showing the uniform formation of the bilayer islands. We can also observe small multilayer regions (a few μm) near the center of the bilayer islands (inset of Figure 4a, Figure S4). At the later stage of 1 + 19 min, graphene fully covered the Cu surface (Figure 4c,d). The typical Raman spectrum of the continuous graphene had an $I_{2D}/I_G \approx 1$, showing that the graphene islands were mostly in bilayer form, and a significantly smaller $I_D/I_G (0.05)$ than that of the 1 + 4 min sample (Figure 4e). The reduced $I_D/I_G$ ratio is possibly due to the carefully grown graphene at a low CH4/H2 ratio in the second step and the reduced effect of the island edges. The Raman spectra showed a similar pattern at most of the other points (Figure S5b). We also observed small multilayer regions (Figure 4d) that are similar in size (a few μm) than those in the 1 + 4 min sample (inset of Figure 4a). The coverage (area ratio) of the multilayer regions was evaluated by Image J software and was found to be 2.5% in the continuous graphene film (Figure 4d). For the six samples synthesized with CVD times between 1 + 4 and 1 + 89 min, five samples were mostly bilayer (Figure S5a,b) and only one sample was mostly single-layer (Figure S5c). The continuous film of mostly single-layer graphene, transferred to a quartz glass substrate, had an optical transmittance of 97.7% at 550 nm in the UV–visible (vis) spectrum (Figure S5d). These results show that the first 1 min nucleation step with a high CH4/H2 ratio promoted nucleation of bilayer graphene possibly due to fast carbon deposition. Once the bilayer islands nucleate, the first and second layers grow at a similar rate in the successive second step with a low CH4/H2 ratio, resulting in uniform bilayer graphene (Figure 4f). However, the multilayer islands, which nucleate possibly at some impurity site of the epitaxial Cu film, grow slowly.

Figure 3. SEM image of graphene synthesized on the epitaxial Cu film (thickness ~3 μm) on the fresh sapphire substrate by one-step CVD with 55 mTorr CH4/37 Torr H2/39 Torr Ar at 1050 °C for 20 min. Red lines are drawn in the same direction as the oriented graphene islands. Blue lines are drawn for the disoriented islands.

Figure 4. Graphene synthesis using the epitaxial Cu film (thickness ~3 μm) on the fresh sapphire substrate by two-step CVD. After annealing under 100 vol % H2 at 1050 °C and 760 Torr for 30 min, the first-step CVD was carried out with 83 mTorr CH4/15 Torr H2/61 Torr Ar at 1000 °C for 1 min and the second-step CVD was successively carried out with 83 mTorr CH4/20 Torr H2/56 Torr Ar at 1000 °C for 4 or 19 min. (a, c) Top-view SEM images of the as-synthesized graphene on Cu. (b, d) Top-view optical microscope (OM) images and (e) Raman spectra with excitation at 488 nm of the graphene transferred to the SiO2/Si substrates. (f) Structure model for graphene. Data were taken from the center of the substrates.
single-layer or bilayer graphene may cover the multilayer sites and prevent the growth of multilayer islands.

Next, we tried to reuse the sapphire substrates for only the Cu epitaxy process (without graphene growth). We deposited Cu on a sapphire substrate by RVD, performed H2 annealing with or without 1 min of CVD. Skipping the graphene growth and transfer steps, we treated the substrate with an FeCl3 solution to remove the Cu (and graphene), annealed the substrate under O2, treated the substrate with a H2O2−H2SO4 mixed solution, and repeated these steps multiple times. The optical images in Figure 5a show that Cu was deposited epitaxially on the same sapphire substrate five times. At the sixth and seventh cycles, the central region remained shiny whereas the outer region became foggy (Figure 5b,c). In the SEM images, the central region had a smooth surface (Figure 5d), similar to the epitaxial Cu film on fresh sapphire (Figure 1e), whereas the outer region showed boundary patterns at the sixth cycle, similar to the nonepitaxial Cu film on the SiO2/Si substrate (Figure 1b). Figure 5f shows the mass decrease of the Cu films through H2-annealing (with or without 1 min of CVD) and surface roughness of the as-deposited Cu films at the different cycles. Roughness was evaluated using the AFM images taken over a 10 × 10 μm2 area at the center of each sample for the first to sixth cycles and at the nonepitaxial part a few mm apart from the center for the seventh cycle.

Figure 5. Reusing a sapphire substrate for Cu epitaxy. (a−c) Optical images of Cu films deposited on the reused sapphire substrate at different cycles with Cu deposited on SiO2/Si as a reference. (d, e) SEM images of the Cu film at the sixth cycle taken before the H2-annealing at the center (d) and the outer region (1 mm from the edge of the substrate) (e). (f) Mass decrease of the Cu films through H2-annealing (with or without 1 min of CVD) and surface roughness of the as-deposited Cu films at the different cycles. Roughness was evaluated using the AFM images taken over a 10 × 10 μm2 area at the center of each sample for the first to sixth cycles and at the nonepitaxial part a few mm apart from the center for the seventh cycle.

Figure 6 shows the AFM images of the Cu surface deposited at the third (a, c) and sixth (b, d) cycles on the reused sapphire substrate. Images were taken at the center of each sample. The upper and lower height scale bars apply for the images before (a, b) and after (c, d) annealing, respectively. The white lines show the direction of the steps.

Figure 6. AFM images of the Cu surface deposited at the third (a, c) and sixth (b, d) cycles on the reused sapphire substrate. Images were taken at the center of each sample. The upper and lower height scale bars apply for the images before (a, b) and after (c, d) annealing, respectively. The white lines show the direction of the steps.

We therefore conclude that the sapphire substrates can be reused for Cu epitaxy up to five times, and maybe more with appropriate treatment of the sapphire surface.

Figure 6 shows the AFM images of the Cu films deposited on the reused sapphire substrate. As explained above (Figure 5), the Cu film had a smooth surface when deposited during the early cycles (Figure 6a) whereas it had a rough surface during the later cycles (Figure 6b). The H2 annealing had a significant effect on the surface structure of the Cu films (Figure 6c,d); their surface roughness decreased significantly (note the different height scale bars) and clear steps with six-fold symmetry appeared. The quality of epitaxy degraded during the later cycles but could be recovered to a certain extent by the H2 annealing.

Next, we examined the reuse of another sapphire substrate in the whole process including graphene growth and transfer to the SiO2/Si substrate. In this set of repeated cycles, epitaxial Cu film was obtained on the sapphire substrate six times, as
confirmed by the out-of-plane, in-plane, and phi-scan XRD measurements (Figure S6a–c) and a continuous graphene film (1.8 × 1.8 cm²) was obtained on a SiO₂/Si substrate by poly(methyl methacrylate) (PMMA)-assisted transfer (Figure S6d). The SEM and OM images (Figure 7a,b) show that the graphene synthesized and transferred to the SiO₂/Si substrate at the third cycle was fairly uniform, and the Raman mapping of I_D/I_G ratio (Figure 7c) shows that the graphene was mostly of bilayer form. The bilayer graphene was Bernal-stacked because its 2D peak was fitted with four Lorentzian peaks (Figure S7).²⁹,³⁰ The reused sapphire substrate yielded continuous graphene films of mixed single-layer and bilayer graphene for the first to seventh cycles (Figure 7d). The graphene films retained their quality in terms of I_D/I_G ratio (<0.1) and sheet resistance (1.2−1.3 kΩ/sq without doping) for the first to seventh cycles (Figure 7e). However, at the seventh cycle, the Cu film did not grow epitaxially on the reused sapphire substrate, resulting in a graphene film with a degraded quality.

Finally, we analyzed the surface of the sapphire substrate that was reused eight times. Micro X-ray photoelectron spectroscopy (μ-XPS) showed Si peaks on both the central region where Cu still grows epitaxially (Figure 8a) and the outer regions where Cu no longer grows epitaxially (Figure 8d) and Cu was removed by FeCl₃ solution, O₂ annealing, and acid treatment. Analysis was done by (a, d) μ-XPS, (b, e) top-view SEM-EDS, and (c, f) AFM.
(Figure 8e,f) than those in the central region (Figure 8b,c). Further, SEM-EDS elemental analysis showed a higher surface content of Si at the outer region (0.27 wt %, Figure 8e) than that at the central region (0.06 wt %, Figure 8b) (EDS acceleration voltage of 10 kV). The particles are probably Si or SiO₂ coming from the reactor tube, accumulating with increasing cycles, and finally inhibiting the epitaxial growth of Cu during RVD. We are now working on the prevention of this contamination and/or effective removal of the particles to reuse sapphire substrates for increased numbers of cycles.

**CONCLUSIONS**

1−3 μm thick epitaxial Cu films were obtained in 10−30 s on a c plane sapphire substrate by RVD with a Cu source heated to temperatures (1700−1800 °C) that are much higher than its melting point (1085 °C). The deposition is 2−3 orders of magnitude faster than the speed of the conventional sputtering method and the resulting epitaxial Cu films had a twinned structure. Low-pressure CVD using CH₄/H₂ yielded continuous graphene films of either bilayer or single-layer form on the epitaxial Cu films. After transferring the graphene to SiO₂/Si substrates, the sapphire substrates were annealed in O₂, treated with acid, and reused for Cu epitaxy and CVD of graphene. Epitaxial Cu films of small surface roughness were repeatedly obtained after 5−6 cycles, yielding graphene of consistent quality (I_D/I_G < 0.1, sheet resistance of 1.2−1.3 kΩ/sq without doping). The sapphire substrate acquired Si or SiO₂ particles, especially at the outer regions, which possibly inhibited the Cu epitaxy during later cycles. Prevention and/or removal of the particles will enable the reuse of sapphire substrates for increased numbers of cycles.

**METHODS**

Preparation of Cu Films on Substrates by RVD. c Plane sapphire (Kyocera, Kyoto, Japan) or SiO₂ (50 nm)/Si substrates (2 × 2 cm²) were pre-treated by dipping into H₂O₂/H₂SO₄ = 1/3 solution for 5 min and rinsing in deionized water. The substrate was dried by N₂ gas blow, set on a quartz glass stage in a vacuum chamber with the substrate surface facing down, and evacuated to 1−5 × 10⁻⁴ Pa by a turbo-molecular pump. Then, a 1−3 μm thick Cu film was deposited on the substrate (heated at 400 °C) by RVD for 10−30 s, by heating of Cu wire (99.9%, 1 mm φ, 20 mm in length, Nilaco; Tokyo, Japan) to 1700−1800 °C using a tungsten boat. During RVD, the pressure in the chamber increased to ∼1 × 10⁻³ Pa due to gas emission from the hot Cu source. The deposited Cu films were analyzed by SEM (Hitachi S-4800; Tokyo, Japan) equipped with EDX (Genesis; AMETEK EDAX, Berwyn, PA), XRD (RINT-Ultima III; Rigaku, Akishima, Japan), and AFM (SPM-9600; SHIMADZU, Kyoto, Japan).

Graphene Growth by CVD. Graphene was grown by a two-step CVD. The Cu/sapphire substrate was loaded in a thermal CVD apparatus consisting of a quartz tube (inner diameter of 34 mm), a furnace (heating zone of 300 mm), and a U-turn gas supply, and heated at a ramping rate of ∼1 °C/s to 1050 °C and held for 30 min under a 760 Torr H₂ flow at 50 sccm. The reactor was then cooled to 1000 °C at a cooling rate of ∼1 °C/s. The graphene growth process was initiated by switching the gas to 83 mTorr CH₄/15 Torr H₂/61 Torr Ar with a total flow rate of 460 sccm. After 1 min, the gas was switched to 83 mTorr CH₄/20 Torr H₂/56 Torr Ar with a total flow rate of 460 sccm and kept for 4−89 min. After the growth step, the reactor was rapidly cooled to room temperature at a cooling rate of ∼10 °C/s.

Transfer of Graphene to the SiO₂/Si Substrate. Onto the graphene/Cu/sapphire sample, 4 wt % PMMA in ethyl lactate solution (100 μL) was spun-coated at 2000 rpm for 1 min, followed by baking at 180 °C for 30 min on a hot plate. The thickness of PMMA was approximately 500 nm. Cu was etched by 1 M FeCl₃ solution (30 mL), and the obtained PMMA/graphene film floating on the solution surface was collected by a SiO₂ (90 nm)/Si or quartz substrate and put into deionized water to be washed. After drying on a hot plate at 80 °C for 30 min, PMMA was removed in acetone (50 mL), and graphene/SiO₂/Si was obtained. The transferred graphene was observed by SEM, UV−vis spectroscopy (V-630; JASCO, Hachioji, Japan), and Raman spectroscopy (HORIBA HR-800; Kyoto, Japan) with an excitation laser wavelength of 488 nm. The 2D peak (∼2700 cm⁻¹) in the Raman spectra was analyzed using PeakFit software (HULINKS Inc., Tokyo, Japan).

**Treatment and Characterization of the Sapphire Substrate for Reuse.** The sapphire substrate after the transfer process was cleaned for reuse; it was annealed in 30 Torr O₂/730 Torr Ar with a total flow rate of 500 sccm at 850 °C for ∼30 min and then treated by dipping into H₂O₂/H₂SO₄ = 1/3 solution for 5 min. Then, the treated sapphire substrate underwent the next cycle, starting with Cu-RVD. The surface of the Cu films on the reused sapphire substrate was analyzed by SEM and AFM before/after H₂-annealing. The surface of the reused sapphire substrate after O₂-annealing and acid treatment was analyzed by SEM-EDS, AFM, and µ-XPS (PHI-5000 VersaProbe II; ULVAC-PHI, Chigasaki, Japan). The sheet resistance of the resulting graphene films was measured by the four-point-probe method after transferring them to the SiO₂/Si substrate.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00509.

Vapor pressure and corresponding maximum deposition rate of Cu for different Cu source temperatures, XRD patterns of the Cu films as-deposited by RVD on sapphire substrates at different substrate temperatures, typical SEM-EDS spectrum of the as-deposited epitaxial Cu film on a sapphire substrate, spatially resolved Raman analysis of a graphene island synthesized in 1 + 4 min by two-step CVD, Raman spectra of graphene taken at multiple points, UV−vis spectrum of the continuous film of mostly single-layer graphene transferred to a quartz glass substrate, XRD patterns of an as-deposited Cu film on a reused sapphire substrate, optical image of PMMA/graphene film transferred to a SiO₂/Si substrate, and Raman 2D peak of the graphene synthesized at the third cycle using the reused substrate (PDF).

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Y.N. conducted most experiments. Y.N. analyzed the results and wrote the paper with H.S. and S.N. A.O. set up the apparatus and optimized conditions for the CVD synthesis of graphene. T.M. made the initial investigation of the rapid Cu epitaxy on plane sapphire substrates. K.H. and H.S. supported and guided the experiments. S.N. conceived the rapid copper epitaxy on and reuse of plane sapphire substrates and supervised this work.

Notes
The authors declare no competing financial interest.

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