

Synthesis of CVD-graphene on rapidly heated copper foils†

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Most chemical vapor deposition (CVD) systems used for graphene growth mainly employ convection and radiation heat transfer between the heating source and the metal catalyst in order to reach the activation temperature of the reaction, which in general leads to a long synthesis time and poor energy efficiency. Here, we report a highly time- and energy-efficient CVD setup, in which the metal catalyst (Cu) is designed to be physically contacted with a heating source to give quick heat transfer by conduction. The induced conduction heating enabled the usual effects of the pretreatment and annealing of Cu (*i.e.*, annihilation of surface defects, impurities, and contaminants) to be achieved in a significantly shorter time compared to conventional CVD. Notably, the rapid heating was observed to lead to larger grains of Cu with high uniformity as compared to the Cu annealed by conventional CVD, which are believed to be beneficial for the growth of high quality graphene. Through this CVD setup, bundles of high quality (~252 Ω per square) and large area (over 16 inch) graphenes were able to be readily synthesized in 40 min in a significantly efficient way. When considering ease of scalability, high energy effectiveness and considerable productivity, our method is expected to be welcomed by industrialists.

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Introduction

It has been continually reported that graphene outperforms the best physical/chemical properties of most conventional materials and that it will achieve unprecedented classes of optoelectronic,¹ electronic^{2,3} and electromechanical devices.⁴ Several commercial applications are being developed with eager anticipation to take advantage of its excellent properties. However, because of several hurdles like mass production and device integration issues, it seems to be still difficult for graphene to join the mainstream electronics market. Even though scientific issues relating to the properties of graphene are consistently resolved, industrialists are waiting to hear comprehensive information which can help them arrive at profitable business decisions. In particular, a synthesis method ensuring the mass production of graphene of a large size and good quality in a cost effective manner remains one of the urgent assignments to be undertaken.⁵ Among the graphene synthesis methods so far

reported, chemical vapor deposition (CVD) has been considered to be a most promising candidate for the production of large sized graphene films.^{6–9} Although CVD has resolved issues of the size limitation of graphene, from a productivity point of view it still has a long way to go. Especially, CVD growth usually takes several hours per process. Previously, in order to reduce production time, microwave plasma,^{10–12} inductive heating¹³ and joule heating^{14–16} have been employed. However, excepting the latter none of these techniques appear adoptable for mass-production. Here, we have demonstrated a time effective CVD process with high productivity and scalability which is likely to satisfy the technical standards required in industry.

Experimental section

Graphene synthesis using conventional thermal CVD

Firstly, 25 μm thick Cu foils (Alfa-Aecer, 99.8%, no. 13382) were inserted into a 2 inch quartz tube, which was heated by a horizontal split-tube furnace. As depicted in Fig. 1, under a pressure of 600 mTorr, the furnace was heated up to around 1000 °C with an Ar (50 sccm)/H₂ (20 sccm) mixture continuously flowing. It took around 60 min. Then under the same conditions, annealing followed for 20 min. Subsequently, growth was performed at the same temperature for 20 min under a flow of a CH₄ (30 sccm)/H₂ (30 sccm) mixture. After growth, the samples were cooled down to room temperature.

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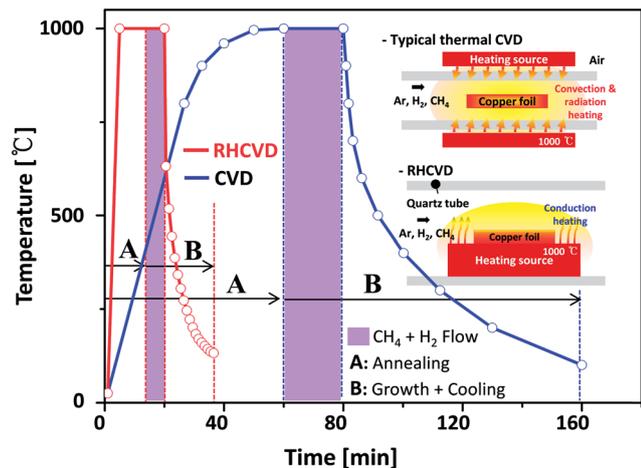


Fig. 1 Comparison of a conventional thermal CVD and a rapid heating CVD (RHCVD) for graphene growth. The plot shows temperature profiles of representative CVD and RHCVD processes. The inset figures highlight the main differences between CVD and RHCVD. Unlike the conventional CVD which typically uses convection and radiation heat transfers for heating up the metal catalysts, in RHCVD, the catalysts were designed to be physically contacted with a heating source to generate and maximize heat transfer by conduction (see details in text).

Wet transfer of graphene

The polymethyl methacrylate (PMMA, Microchem, Inc. 950 A2) was spin coated at 3000 rpm on the graphene/Cu samples. To etch Cu, the PMMA coated samples were submerged in FeCl_3 (Transene, Inc. CE-100) solution for 30 min. After rinsing with deionized water several times, the PMMA/graphene samples floating on deionized water in a flat beaker were fished out onto a SiO_2 (300 nm)/Si glass slide or onto PET substrates. The samples were dried in air for 30 min and then kept in a vacuum oven ($\sim 10^{-2}$ Torr, 70°C) for 60 min in order to remove the water between the substrates and graphenes.

Roll based transfer of graphene

The 16 inch graphene/PET films were prepared based on a roll transfer scheme reported by Bae *et al.*² Firstly, the as-grown graphenes were glued onto thermal release tapes (Nitto, REVALPHA®) by passing between two rollers. This was followed by the etching of Cu using aqueous ammonium persulphate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) solution with nitric acid (HNO_3) for the enhancement of sheet resistance. Then the graphenes were transferred from the thermal release tapes onto the target PET substrate by passing between two rollers at a temperature of 120°C .

Graphene synthesis using RHCVD

A home-made rapid heating apparatus comprised of tungsten filaments and square tubings made by clear and heat-resistant fused quartz was constructed. The flat Cu foils were mounted onto the surfaces of the square tubings, paying attention so that the foil was physically well contacted with the tubings. Then,

the rapid heating apparatus with the Cu foils was mounted into the quartz tube prior to providing a gas flow. The quartz tube was inserted into a home-made control chamber in which electricity, temperature, and flow rates are controllable. For growth, firstly, both 20 sccm H_2 and 50 sccm Ar were supplied to the chamber, and at a pressure of 600 mTorr the Cu foils were rapidly heated up to around 1000°C and maintained for 5, 15 and 25 min, respectively, for the control experiments. Then, under an identical pressure and temperature, CH_4 (20 sccm) gas was injected into the quartz tube for 5, 10 and 15 min, respectively. Subsequently, the rapid heating apparatus was cooled down to room temperature. In order to produce large area graphenes (16 inch), the rapid heating apparatus and the control chamber were simply scaled up. The control chamber was designed to be able to mount many heating apparatus units. Similar processing conditions were applied for large area graphene growth.

Characterization

The surface morphologies of the samples were investigated by field emission SEM (JEOL, JSM-7000F). Raman spectroscopy was done with a laser wavelength of 514 nm and a $100\times$ objective (Renishaw) in order to characterize the graphene on Cu or when transferred onto the substrate. The AFM images were taken by NanoWizard (JPK Instrument) at a 10 nN contact mode with a 0.5 Hz scan rate. The AFM scans for different samples and locations were repeated over 10 times in order to obtain reasonable roughness values. The EBSD patterns were measured by an automated system (Oxford Inc., INCA Crystal C 7468) attached in a FEG-SEM (JEOL, JSM-5600F thermal field emission gun type). The sheet resistances of the graphenes were measured by a four-point probe analyzer (DASOL ENG, RS8-1G). For the identification of the impurity particles, the cross section samples were prepared by a focused ion beam (FEI, Nova 200) and the element analyses were done by TEM-EDX (JEOL, JEM-ARM200F) and an X-ray photoelectron spectrometer (Thermo, MultiLab 2000).

Results and discussion

In general, CVD for graphene synthesis consists of following steps: the pre-treatment (annealing) of metal catalysts like Ni and Cu, the introduction of precursors (*e.g.* CH_4 , H_2) into a reactor (usually a quartz tube), the precursor pyrolysis that forms carbon, and the formation of the graphene from the dissociated carbon atoms. The annealing under a hydrogen atmosphere is performed in order to reach the activation temperature of the reaction, and reduces the surface roughness of the used metal catalysts and enlarges the grain size of the crystals for uniform graphene growth.¹⁷ In addition, the native oxides (CuO , CuO_2) on the as-received Cu, which reduce its catalytic activity, can be removed by annealing, which also leads to the annihilation of most of the surface defects, volatile impurities, and contaminants that might be present.¹⁸ Typically the Cu foils are annealed over a few hours including the pre-annealing time,^{2,4,9,10,17,18} although a shorter treatment has

been applied for Cu films of a few nanometers thick.^{19,20} In most CVD setups, the catalysts are designed to be heated up by convection and radiation heat transfer between the catalyst and the environment in a quartz tube enveloped by a split furnace. The time required to reach the reaction temperature accounts for a great part of the total operation time of the synthesis (Fig. 1). Even at the laboratory scale, the synthesis of CVD graphene takes a few hours. Taking into account the high thermal conductivity of the Cu catalyst, once the CVD reactor is designed to effectively utilize heat transfer by conduction in the process, the synthesis time can be greatly reduced and the productivity (time-effectiveness) of the graphene can be increased. Consequently, this would be technologically of great benefit. As depicted in the inset of Fig. 1, we have devised a CVD setup which has adopted heat transfer by conduction together with convection and radiation. Unlike a common CVD reactor, the metal catalyst (Cu) with a thickness of 25 μm was designed to be physically contacted with a rapid heating source (hereinafter called the "RHCVD": Rapid Heating CVD), thereby minimizing unwanted thermal energy loss and promoting direct heating through conduction.

As a first experiment (Fig. 2a), after a fixed short annealing time (5 min including the time needed to reach 1000 $^{\circ}\text{C}$) under a H_2 flow, graphene was synthesized with different growth times (5, 10, and 15 min, respectively). Cu foils were prepared by electroplating and were typically covered with a layer of oxides for anticorrosion. Impurities inside the Cu foils²¹ can be removed through annealing. Due to the short annealing time applied, it was expected that the synthesized graphene would show poor quality or even no growth, considering the importance and role of the annealing process that is repeatedly emphasized in the literature. However, even under conditions of 5 min annealing and 5 min growth (G(5, 5)), the graphenes were successfully synthesized, although the graphenes contained a high defect density, as can be seen from the D peak in the Raman spectra (Fig. 2b and c). Sheet resistances measured after transferring onto a SiO_2 (300 nm)/Si substrate were observed to be in the range of a few thousand and several hundreds of Ω per square. The graphene synthesized with the longer growth time (G(5,15)) showed the lowest and comparable resistance values to graphene synthesized with a conventional thermal CVD with a long synthesis time (over 2 h). The general qualities evaluated by a comparison of the Raman peak

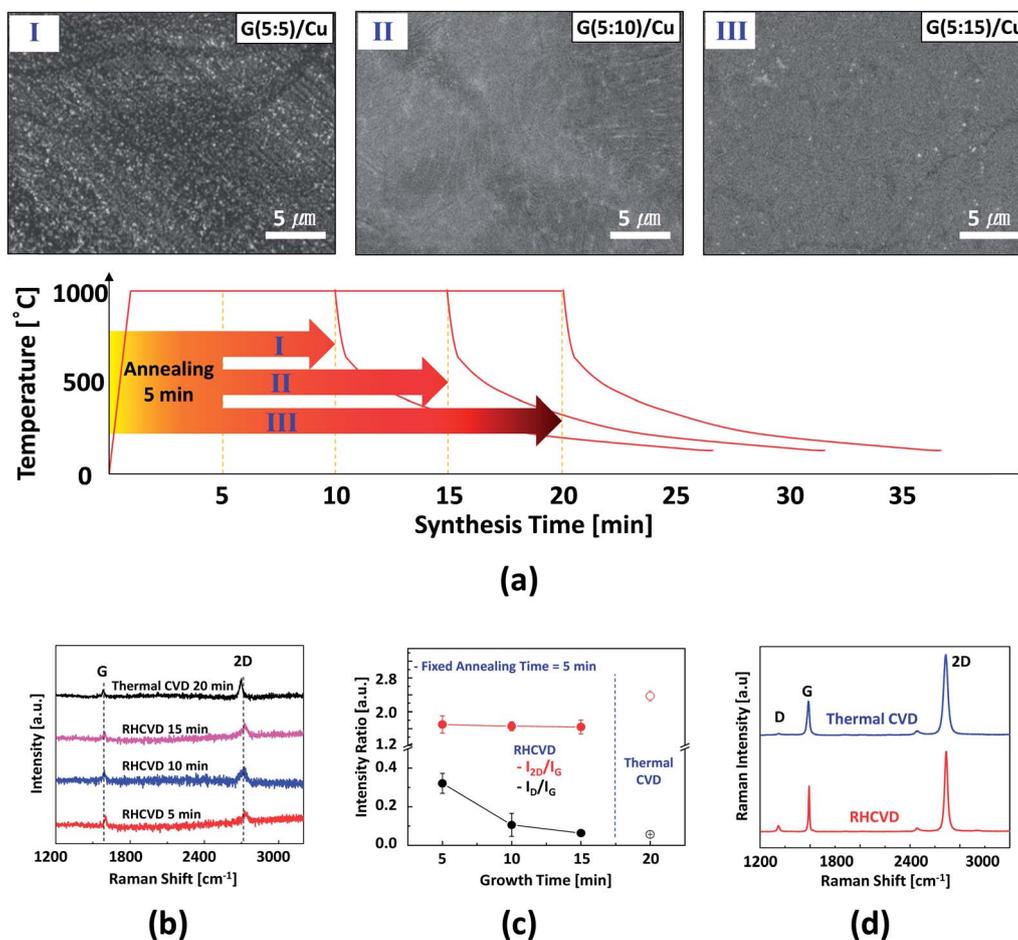


Fig. 2 Graphene synthesized by RHCVD with a fixed annealing time. (a) Temperature profiles of samples I, II and III and corresponding representative SEM images. (b) Raman point spectra of the selected locations on the samples with G and 2D bands indicated. (c) The intensity ratios of I_{2D}/I_G and I_D/I_G with respect to the growth time. (d) Comparison of Raman spectra of the graphenes synthesized by RHCVD and CVD.

intensity ratios also showed similar trends, *i.e.*, $(I_D/I_G)_{\text{RHCVD}} \approx (I_D/I_G)_{\text{CVD}}$ (Fig. 2d). When comparing the morphologies of the graphene films grown on Cu with different growth times, it was observed that the longer the growth time is, the smoother the surface is (SEM [scanning electron microscope] images in Fig. 2a). The graphene films grown with a shorter growth time appeared to have more contaminants or impurities (white colored particles in the SEM images). One may think that those particles are mostly the reduced oxides from the raw Cu foils which are formed due to insufficient annealing/growth time. However, it turned out that these particles come from another source and the short annealing/growth time applied here is likely to be sufficient for graphene growth, as can be further deduced from the results shown in Fig. 3.

As a second control experiment the graphene was synthesized by varying the annealing times (5, 15 and 25 min, respectively) and fixing the growth time (15 min). In contrast to the morphology changes with a variation of growth time, an increase of the annealing time was observed to give rise to a noticeable reduction of the contaminants or impurity particles (Fig. 3a). These particles are verified to be foreign impurities in contrast to their assumed identity, *i.e.* residues of native materials which already existed in the raw Cu foil. As can be seen from the TEM-EDX (transmission electron microscope-energy dispersive X-ray spectroscopy) data (Fig. 3b), measured

from a sample of a cross-sectioned single particle, one of the main elements of the impurity particles was shown to be silicon (Si). The XPS (X-ray photoelectron spectroscopy) results confirmed the existence and distribution of Si on the graphene/Cu (Fig. 3c). Considering the decrease of the Si impurities with an increasing annealing time, it is thought that the Si was presumably introduced from the inlet of the quartz tube reactor used when the raw Cu foil was loaded into the reactor for the growth process.²² Because a split-tube furnace with a reaction tube made by Pyrex, alumina, fused silica, *etc.* has been widely used for graphene growth, it is worth mentioning that one should bear in mind the possibility of sample contamination and pay special attention to the sample loading. The density of the impurities was naturally assumed to cause a deterioration of the resulting graphene quality, as can be clearly seen from the SEM images and the corresponding electrical sheet resistance variations in Fig. 3a. In particular, the impurities appeared to bring about another adverse effect. Namely, the impurities induced undesirable damage like tears and holes in the graphene (marked with red arrows in Fig. 3d and e) when transferred to the arbitrary substrate. The shorter annealing time gave rise to more impurities on the graphene, which led to more damage during the transfer process, as compared to the graphene synthesized with a longer annealing time. Thus, the resulting graphene on the SiO₂(300 nm)/Si substrates showed

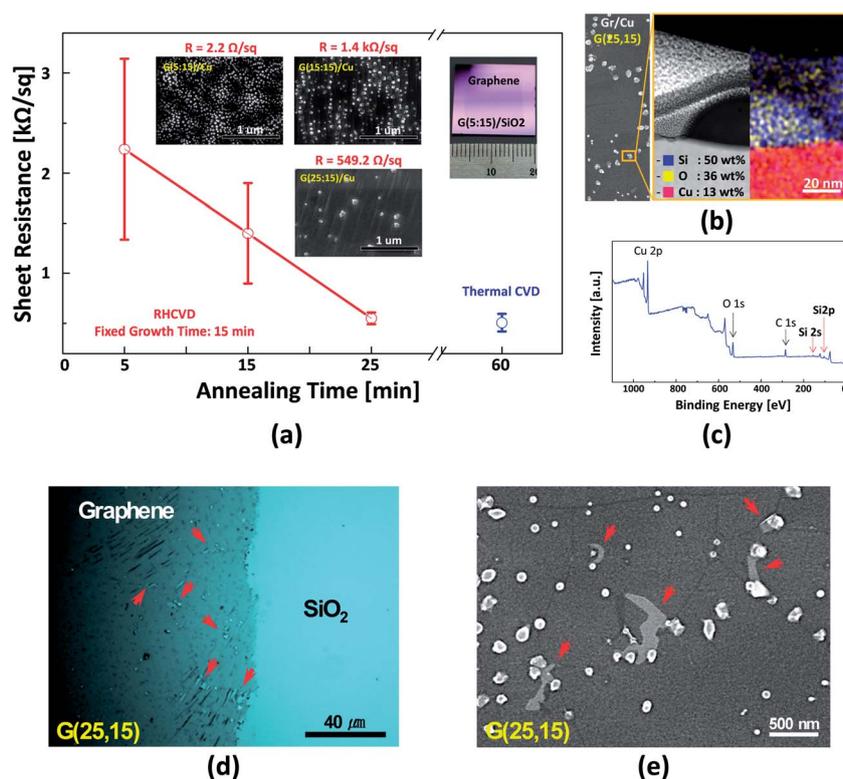


Fig. 3 Graphene synthesized by RHCVD with a fixed growth time. (a) A graph of electrical sheet resistance versus annealing time. The insets are SEM images of the representative as-grown graphene samples. The bottom left picture shows graphene transferred onto a SiO₂ (300 nm)/Si substrate using a wet transfer method. For the identification of the white particles shown in the SEM images, TEM and EDX element analysis (b) as well as XPS measurements (c) were performed. (d and e) Optical microscope and SEM images observed after transferring the graphenes onto a SiO₂ (300 nm)/Si substrate (see details in text).

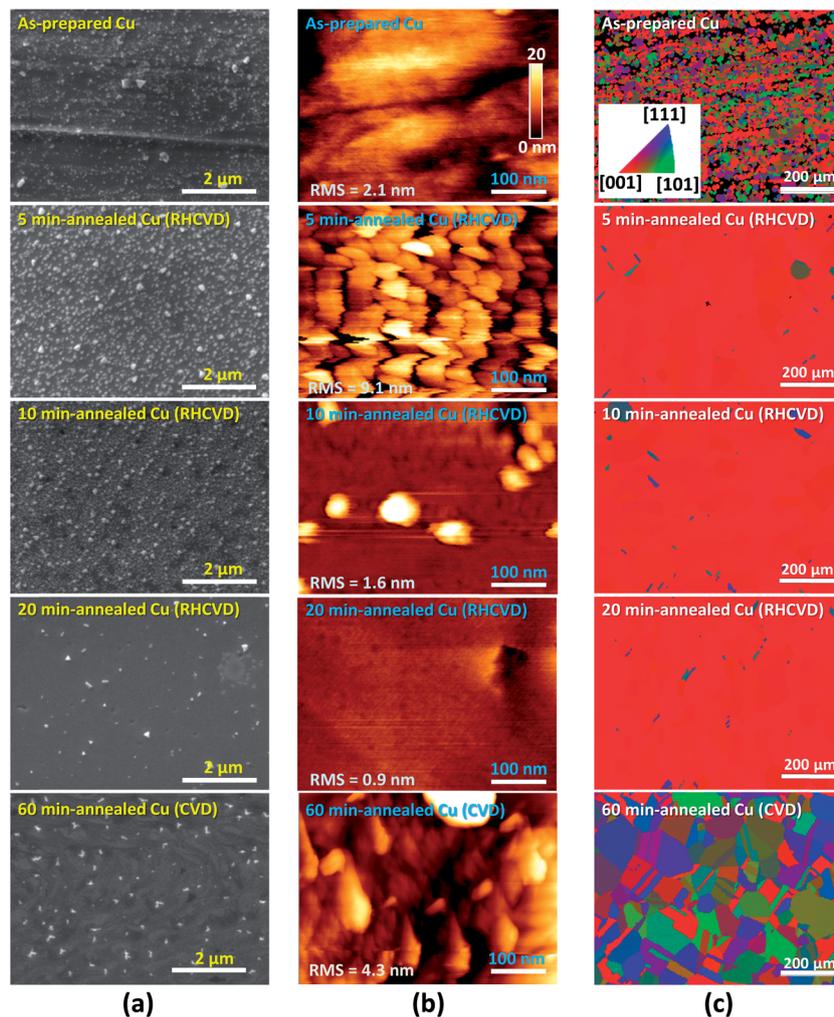


Fig. 4 Comparison of annealing effects produced by RHCVD and CVD. In order to compare the evolution behavior of the surface morphology, surface roughness and microstructure of the Cu foils, (a) SEM, (b) AFM, and (c) EBSD analyses were performed right after annealing (at around 1000 °C) for 5–20 min by RHCVD, and for 60 min by CVD, respectively. The inset in the EBSD map of the as-prepared Cu (uppermost image of (c)) shows the corresponding inverse pole figure.

a comparatively high electrical sheet resistance. It is thought that the quality of the graphene can be greatly improved, provided that the impurity input can be reasonably controlled. Taking our observation into consideration that a longer annealing time (more than 25 min) did not lead to any further reduction of impurities and improvement in sheet resistance, 25 min was thought to be a threshold annealing time. As a result, it was found that, through the RHCVD process of using conduction heating, it would take only 40 min (*i.e.* G(15, 25): 15 min annealing, 25 min growth) to produce graphene with a comparable quality to that synthesized by the typical CVD process using convection and radiation heat transfer. It is noteworthy that the 15 min annealing time is enough for the growth of graphene with reasonable quality.

The typical CVD process usually takes a few hours and the annealing process consumes most of this time and energy. Thus, the annealing method can be regarded as the bottleneck in terms of energy economy and productivity improvement.

Because the RHCVD system used here adopted a high heating rate with conduction heating *via* direct physical contact between the heating source and Cu with very high thermal conductivity, it is obvious that RHCVD has a better time and energy effectiveness than the CVD in the perspective of heat transfer. Furthermore, it was also observed that conduction heating is a more effective means to reduce surface roughness and to induce recrystallization of the Cu catalyst in a short period of time (Fig. 4). In the case of the conventional CVD, it took over 60 min to reduce contaminants on the Cu surface, while the RHCVD produced an even better quality of Cu within 20 min (Fig. 4a). In addition, as can be seen in Fig. 4b, the surface of the Cu annealed by RHCVD ($\text{RMS} \approx 0.9 \text{ nm}$) was far smoother than that given by CVD ($\text{RMS} \approx 4.3 \text{ nm}$). Another notable observation was the different recrystallization behaviors of Cu, as can be seen in the EBSD (electron backscatter diffraction) maps (Fig. 4c) representing the surface microstructure. The as-prepared (purchased) Cu revealed a highly

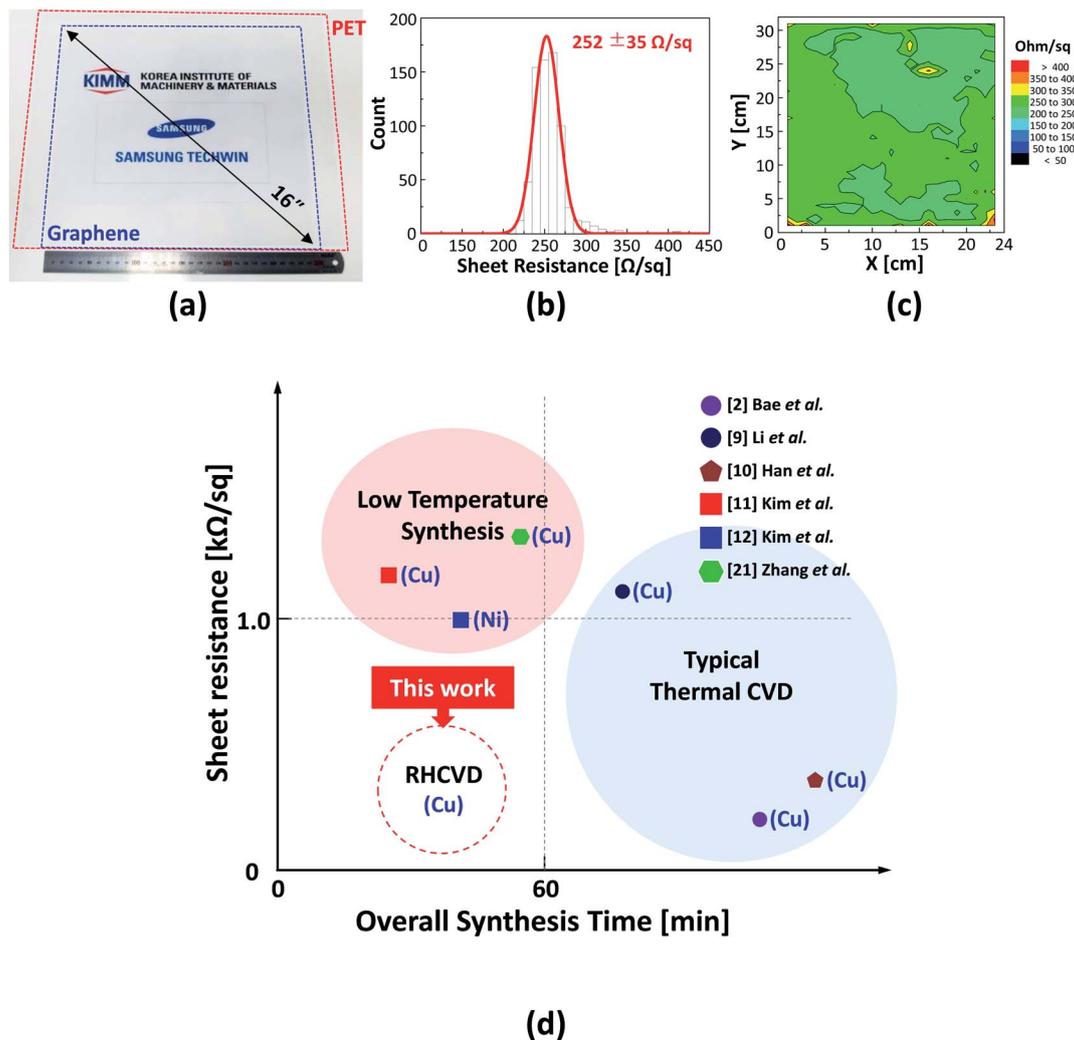


Fig. 5 Preliminary results for the commercial scale production of graphene. Through the enlarged RHCVD system, dozens of graphenes were simultaneously synthesized in 40 min. (a) A transparent graphene film on a 16 inch PET substrate which was transferred by a roll based transfer method.² (b) Distribution of electrical sheet resistances measured on 713 points on the graphene/PET sheet. (c) Sheet resistance map of the graphene film shown in (a). (d) Comparison of RHCVD with other CVD methods from the viewpoint of productivity and an electrical property.

polycrystalline nature. After annealing for 60 min by CVD, the Cu showed a less polycrystalline nature, however it still shows a number of grains with a slightly enlarged size. In contrast, in the case of the RHCVD, even after annealing for 5 min, most of the grains on the Cu surface were observed to have (001) planes. Notably, the RHCVD led to significantly larger Cu grains of the size of a few millimeters as compared to the conventional CVD (Fig. S1†). Presumably, this is related to a grain coarsening mechanism by rapid heating.²³ As mentioned, by increasing the annealing time, one has reduced contaminants, impurities, and defects on the catalytic Cu surface, thereby suppressing the graphene nucleation and consequently producing high quality graphene.¹⁸ It has also been reported that a flat surface morphology (low roughness) of the used Cu catalyst leads to enhanced homogeneity and improved electronic transport properties of the resulting graphene,²⁴ and that Cu with low Miller index planes produces more monolayer graphenes with fewer defects.¹⁷ Additionally, larger Cu grains generally ensure

uniformity of the grown graphene. On the basis of these facts and our observations, the RHCVD process is believed to show superior productivity of the high quality graphene compared to most methods reported so far.

The lab scale RHCVD presented here certainly revealed several attractive advantages including energy saving efficiency. This led us to scale up the RHCVD setup to be able to mass-produce large area graphene. Recently, our group has been developing a commercial scale RHCVD and optimizing the processes, aiming to produce and commercialize graphene based display applications. Presently, dozens of graphene films over 16 inches in size can be simultaneously produced with one RHCVD process taking less than 40 min (Fig. 5a). The electrical sheet resistance of the resulting graphene films transferred onto a PET (polyethylene terephthalate) substrate is currently in the range of $\sim 252 \Omega$ per square and the films show quite a uniform distribution (Fig. 5b and c). The quality and uniformity are expected to be continuously improved. Fig. 5d shows

the relative comparison of RHCVD with other graphene synthesis methods introduced in the literature in terms of productivity (time-effectiveness) and quality (sheet resistance). Our RHCVD method shows a higher productivity than the typical CVD, and the resulting graphenes show a comparable sheet resistance. In comparison to a low temperature CVD with plasma treatment,¹¹ the qualities of the resulting graphenes were shown to be better. Taking into account the fact that the roll-to-roll production based on the Joule heating method¹⁶ is nearly three times faster in producing a similar amount of graphene, it would be a better choice from the productivity point of view. However, it is believed that the productivity of the RHCVD can be improved by increasing the number of the accumulated RHCVD modules in a single piece of equipment.

Concluding remarks

In contrast to a conventional CVD process for graphene growth which in general heats the metal catalyst (Cu) mainly by convection and radiation heating, here we have demonstrated a rapid heating CVD process in which the Cu is allowed to be in direct contact with a rapid heating source. The conduction based heating was found to be greatly beneficial in terms of the surface treatment and microstructure changes of the Cu, as compared to the conventional CVD. Furthermore, the high thermal conductivity of Cu led to a significantly reduced processing time, and the resulting graphenes showed a high uniformity as well as comparable sheet resistance values to the graphene synthesized by conventional CVD. Thanks to its time and energy saving effectiveness as well as scalability, in the near future this method could be adopted in industry as a promising method for the mass production of graphene.

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