



Study of solid carbon source-based graphene growth directly on SiO₂ substrate with Cu or Cu/Ni as the sacrificial catalysts

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Abstract

Herein, we report the results of directly synthesizing wafer-scale graphene on silicon dioxide surface using the photoresist based and Cu and Cu/Ni thin-film coating-assisted chemical vapor deposition method. A systematical investigation of the effects of growth condition, such as temperature, time, and metal catalyst layer of Cu and Cu/Ni, on the growth of graphene have been conducted. Multi-layer graphene films are prone to be grown using the Cu/Ni capping layer, while monolayer graphene films are produced using the Cu capping layer. The results demonstrate that such simple method using solid phase photoresist as carbon feedstock can provide a practical route to realize large-scale and mass production of monolayer graphene on dielectric substrate no need of conventional transfer procedure. It sheds a light on future graphene electronic industry.

Introduction

The thin-film graphitic material with graphene like structure was known as early as the 1960s,^[1] and several theoretical works already predicted the electronic structure of single-layer hexagonal carbon layer;^[2–4] however, until 2004, the experimental demonstrations of its extraordinary electronic properties were reported.^[5–7] Ever since and up to now, the research on graphene has always been considered as a hot topic in seeking new material candidate for the next generation integrated circuit due to its extraordinary physical and transport properties.^[8–12] In general, mainstream graphene growth methods including mechanical exfoliation,^[5] epitaxial graphene growth on SiC,^[13] oxidation reduction from graphene oxide^[14], and chemical vapor deposition using carbon-enriched materials as feedstock.^[15–18] Among these methods, transition metal substrate-based, such as Cu and Ni, CVD methods have been viewed as the most promising one for preparing large-scale single-crystal industry-grade graphene due to its simplicity and low cost.^[17–21] However, such graphene must be transferred onto insulating substrates in order to be applied for making useful electronic devices, which inevitably introduces large amounts of contaminations and defects.^[22] Therefore, developing a relevant approach that can direct growth graphene on insulating substrate is pressing needed due to its great potential applications.^[23]

Recently, much efforts have been devoted to the direct graphene growth on insulating substrates.^[24–27] However, the high-quality, uniform, and large-area graphene film growth is still extremely challenging.^[28–31] As one of them, by spin-coating polymer on an insulating substrate as the carbon source

combined with the atop deposited thin sacrificial metal film was considered as the simplest and effective way for graphene growth.^[32,33] However, up to now, most of studies have only focused on Ni metal as the capping layer,^[34–40] and a very few on Cu or Cu/Ni as the capping layer.^[41] Considering the vast progress of Cu foil based large-area monolayer single-crystal CVD graphene growth recently,^[42–46] a systematically study of Cu as topping layer in such methods is necessary.

Here, we present a systematically exploration of the correlation between the growth temperature, time, and related parameters of toping Cu/CuNi and the quality of grown graphene, aiming for large-area graphene films directly grown on insulating SiO₂ substrate. The results show that the optimized method greatly reduces the usage of metal comparing to the traditional CVD and completely eliminate the graphene transfer process, which provides a promising candidate for high-quality graphene mass production in industrial.

Experimental section

Synthesis of graphene on SiO₂ substrate

The photoresist of AZ5214E was used as the carbon source and the highly n-doped (ρ 0.01–0.05 Ω cm) Si (100) wafer with a 285-nm SiO₂ layer was used substrate. The substrate was purchased from Hefei Kejing Materials Technology Co., LTD. (Hefei, China). Before graphene growth, the substrates were cut into small pieces of 10 × 10 mm first and supersonically cleaned by acetone, ethanol, and deionized water sequentially about 15 min for each step and then dried with N₂ gas. Photoresist AZ5214E was dissolved in methoxy-propyl acetate

(PGMEA) with a solid content of 28.3% before it was spin coated onto the substrates. The thickness of coating photoresist layer can be finely tuned by the solution concentration, spin-coating speed and time, consequently the total amount of the introduced carbon feedstock for graphene growth. The thickness of the photoresist of 1.4 μm was reached with spin-coating speed of 500 rpm for 5 s and 4000 rpm for 45 s. With the same parameters, for high-quality monolayer graphene growth, the receipt of photoresist is to dilute a drop of photoresist with 20 ml isopropanol, whereas the thickness of photoresist will be reduced to about 10 nm. Subsequently, Cu and Cu/Ni films are coated on photoresist layer through electron beam evaporation to form the sandwich structural sample of Cu/AZ5214E/SiO₂ or Cu/Ni/AZ5214E/SiO₂. For graphene growth, those prepared samples will be put into a corundum boat and inserted into a horizontal CVD furnace with a quartz tube with dimension of 1200 mm $\times$ Φ 60 mm. The explored ranges of growth parameters are: temperature from 900°C to 1100°C and time from 1 to 60 min with constant Ar/H₂ flow at the rate of 50 and 10 sccm, respectively. Finally, the metal film is etched away using FeCl₃ solution.

General characterization

In order to evaluate the quality of the prepared graphene, its surface morphology was characterized by optical microscope (Leica DM2700), atomic force microscope (AFM, Park System NX10) in non-contact mode, and scanning electron microscope (SEM, Hitachi SU3500) under 5-kV beam energy with a secondary electron detector. The thickness and quality were characterized using Raman spectrometer with wavelength of wavelength of 532 nm and beam spot diameter of 1 μm and power of 5 mW (Fig. 1).

Results and discussion

In order to explore the influence of thickness of the deposited Cu film on the grown graphene, a series of thickness have been investigated, including 50 nm, 100 nm, 150 nm, 200 nm, and 250 nm, with Ar/H₂ mixture 50/10 sccm and 15-min growth time at temperature of 1050°C. The Raman spectra reveal that the one with 50-nm Cu film yields the graphene with the highest quality,^[47,48] as shown in Fig. S1. It is noticeable that Raman peaks of graphene were not observed on the top of Cu capping layer; it indicates that no graphene was formed on the top of Cu layer.

The CVD growth temperature is one of the most crucial factors on graphene nucleation and growth. The detailed investigations on its surface kinetics show that increasing the reaction temperature accelerates the growth rate of the CVD graphene film.^[49,50] It is believed that graphene nucleation density decreases at higher temperatures.^[49,51,52] Earlier report suggested that rising the CVD process temperature will lead to a decrease of the substrate's surface roughness, which reduces the active sites for nucleation and improves the mobility of the active species.^[51] Upon

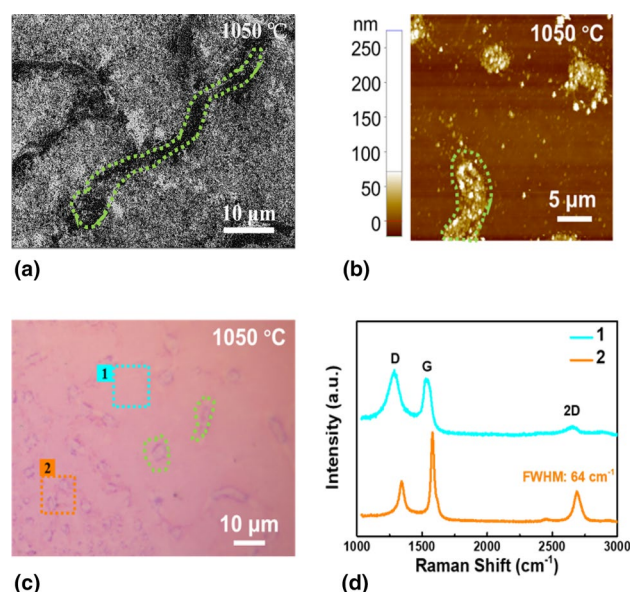


Figure 1. Graphene growth at 1050°C with 15 min and the Ar/H₂ gases ratio is 50/10 sccm. (a), (b), and (c) show the SEM, AFM, and optical microscope images, graphene seeds can be clearly seen after etching the top Cu layer; (d) the Raman spectra of the synthesized graphene flakes at position 1 and position 2 in the optical microscope image. D, G, and 2D Raman peaks are observed at the position of 1343 cm⁻¹, 1580 cm⁻¹, and 2692 cm⁻¹, respectively. The full width at half maximum (FWHM) of the 2D peak is about 64 cm⁻¹, and the intensity ratio of 2D and G peak for I_{2D}/I_G is 1.71. Compared with the previous reports, the grown graphene is considered as consist of approximately five layers.^[14]

the rapid dehydrogenation rate of the hydrocarbon feedstock and/or to the improved probability that active carbon species have on the sufficient energy needed to surmount the energy barrier and attach to the surface for the growth of the graphene film which also favorite the increase of temperature.^[50,53–55]

To investigate the temperature dependence of grown graphene in this case, sequence of temperatures ($T = 900^\circ\text{C}$, 1000°C , 1050°C , and 1100°C) have been tested with the same thickness of Cu film (50 nm) and growth time of 15 min. The Raman spectra of resulted samples are shown as in Fig. 2(a). It shows only the strong D and G peaks when the growth temperature is 900°C, which indicates the formation of amorphous carbon but no graphene.^[47] When the growth temperature is exceeded to 1000°C, D, G, and 2D peaks are observed at 1330 cm⁻¹, 1580 cm⁻¹, and 2700 cm⁻¹, respectively. When it reaches 1050°C, the intensity ratio between 2D peak and G peak I_{2D}/I_G increases, indicating the less stacking of graphene layers and improved crystallinity.^[48,56] For $T = 1100^\circ\text{C}$, a sharp and symmetric 2D peak with the FWHM of 31 cm⁻¹, which indicates its high crystallinity and being monolayer. Hence, we conclude that the higher growth temperature will lead to higher quality of grown graphene; it also coincides with the optical and SEM microscopic images as shown in Fig. 2(c) and (d).

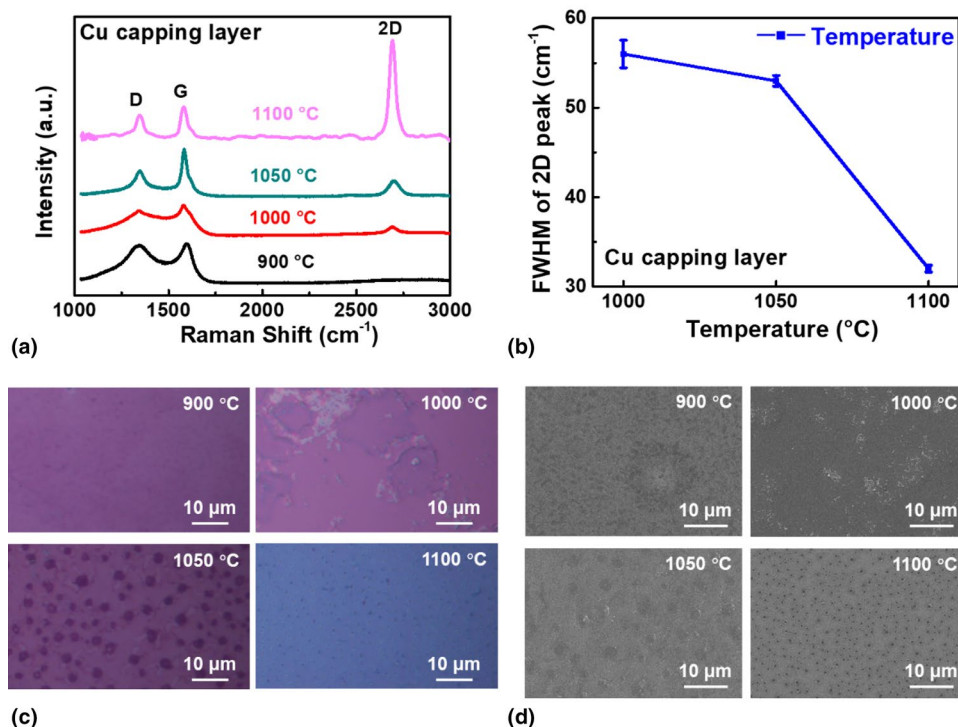


Figure 2. Temperature-dependent growth of the graphene films on SiO₂ substrate for 50-nm Cu capping layer catalyst. (a) Raman spectra of the directly grown graphene on SiO₂ under four various annealing temperatures of 900 °C, 1000 °C, 1050 °C, and 1100 °C with Ar/H₂=50/10 sccm for 15 min after etching the top Cu capping layer. (b) The FWHM of graphene 2D peaks as a function of the growth temperature. (c) Optical microscope images and (d) SEM images of graphene structure corresponding to the Raman spectra.

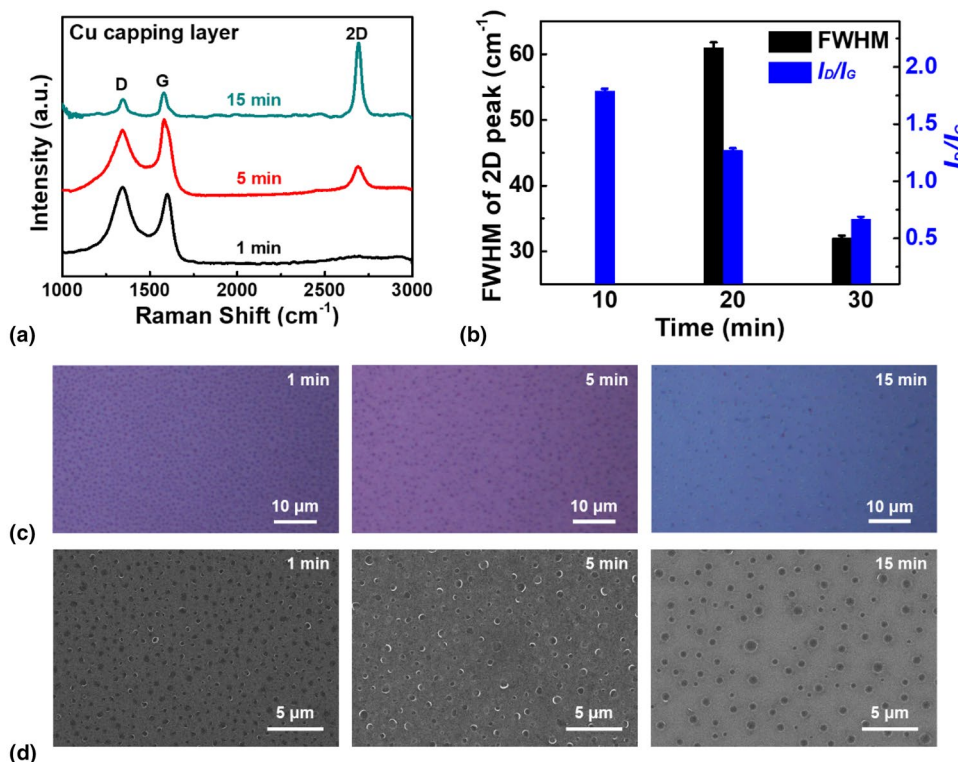


Figure 3. Time-dependent growth of the graphene films on SiO₂ substrate for 50-nm Cu capping layer catalyst. (a) Raman spectra of the directly grown graphene on SiO₂/Si with three different annealing times of 1 min, 5 min, and 15 min, respectively, at 1100 °C with Ar/H₂=50/10 sccm after etching the top Cu capping layer. (b) Histogram of the trend of the FWHM of graphene 2D peaks and I_D/I_G with the growth time. (c) Optical microscope images and (d) SEM images of graphene structure corresponding to the Raman spectra.

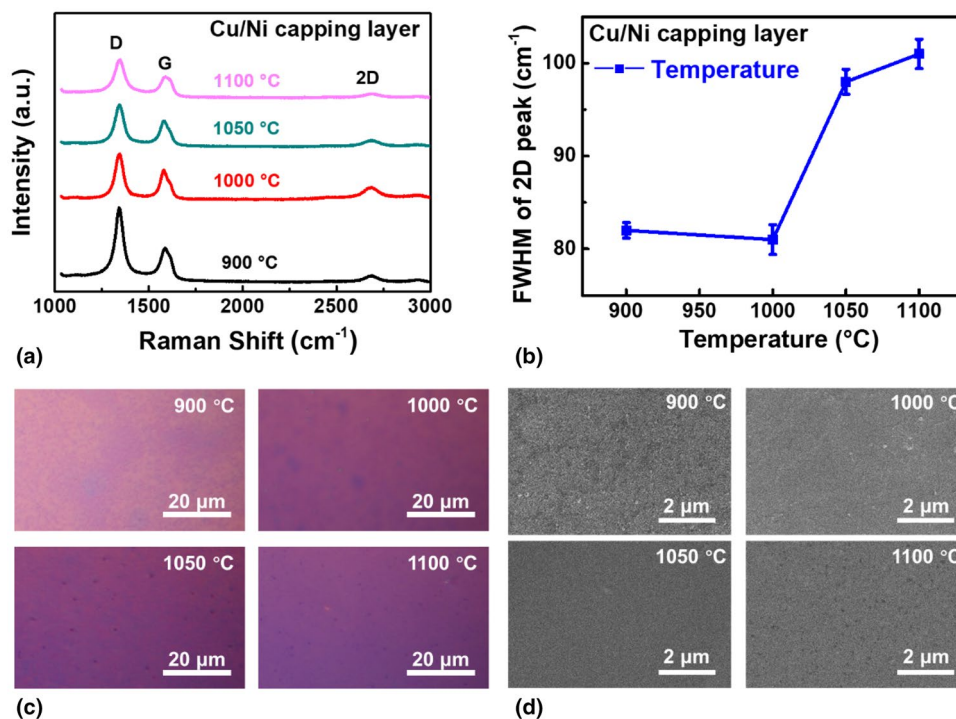


Figure 4. Temperature-dependent growth of the graphene films on SiO_2 substrate for Cu/Ni (50/200 nm) capping layer catalyst. (a) Raman spectra of the directly grown graphene on SiO_2/Si after etching the top Cu/Ni layer at four different annealing temperatures of 1000°C, 1050°C, and 1100°C with $\text{Ar}/\text{H}_2=50/10$ sccm for 60 min after etching the top Cu/Ni capping layer. (b) The FWHM of graphene 2D peaks as a function of the growth temperature. (c) Optical microscope images and (d) SEM images of graphene structure corresponding to the Raman spectra.

The effect of growth time was further studied, the measured Raman spectra of samples are shown in Fig. 3(a), and the processing time is 1 min, 5 min, and 15 min. The results show that only amorphous carbon was formed if the growth time is equal or less than 1 min, while the appearance of the weak 2D peak after 5-min heating indicating the formation of graphene but with poor crystallization evaluated by the rather high $I_D/I_G=1.79$. When the growth time was extended, the sharp and symmetrical 2D peak in Raman with the FWHM of 2D peak of 31 cm^{-1} signals and $I_D/I_G=0.67$ indicate the realizing of monolayer and high crystallinity graphene, as shown in Fig. 3(b). These results reveal that the graphitization process of photoresist can be divided into the two sequential steps of carbonization and graphene formation in this CVD graphene growth procedure with the time extension.^[37] It is worth noting that there are dark circular areas on every grown sample, and they are aggregated carbon particles along copper particles forming in the high temperature annealing process. With the increase of heating time, the amount of such rings gradually decreased due to the hydrogen etching effect on graphitic materials.^[57]

As an alternative, Cu/Ni (50/200 nm) was employed to making the metal thin film on the photoresist. It has lower graphene growth temperature at 1000°C than that using pure Cu capping layer. Figure 4(a) shows the Raman spectra of graphene directly grown on SiO_2 after etching off the Cu/Ni capping layer which

were grown at temperatures of 900°C, 1000°C, 1050°C, and 1100°C. Comparing to the one using Cu atop layer, the sizes of graphene flakes are smaller and most of them are multi-layer. Figure 4(b) shows the FWHM of the 2D peak obtained at different temperatures by Lorentz fitting. The smallest FWHM of 2D peak is about 80 cm^{-1} at 1000°C. The graphene quality also exhibits the similar temperature dependence, but the size of graphene does not significantly change. However, when temperature rises above to 1050 oC, the surface becomes disordered again.

Moreover, growing time dependence of graphene quality have been explored, Raman spectra and SEM characterizations demonstrate that the optimal time is about 30 min, as shown in Fig. S2. Further Raman mapping results verified the fairly good uniformity of grown graphene film as demonstrated in Fig. S3(e–f).

The mechanism of direct growth of graphene on insulating substrates using thin metal film as the capping layer and photoresist as the carbon source have been proposed before.^[38,58,59] It can be summarized as following: (1) Cu as the metal thin film serves as catalyst, the decomposition of PMMA occurs on the lower surface of copper with temperature rising, and subsequently, the produced carbon will reassemble into graphene on both the top of insulator substrate and the lower surface of copper film in the cooling process. The graphene patches

appear on the top surface of copper film is yielded from the precipitation of dissolved carbon of the copper^[38,60]; (2) in the case of nickel film, the nickel plays a role as an excellent solid state solution of carbon to dissolve the PMMA converted amorphous carbon with heating, followed by the crystallization of the carbon precipitation into graphene during the cooling process.^[61,62] (3) Regarding the Ni/Cu alloy film, the above two processes coexist, but with the fine tunability on the interaction between graphene and metal surfaces during different growth stages through doping metal surfaces with impurities or forming metal alloys, consequently, realizing the precisely tuning of graphene growth.

Conclusion

Systematical investigations of direct growth of graphene on an insulating substrate (SiO₂) have been conducted using CVD method with solid carbon feedstock. High coverage of graphene films has been obtained with growth parameters of 50 nm thick Cu capping layer and 10-nm photoresist. It also shows the monolayer graphene growth preference of Cu capping layer and multi-layer of the Cu/Ni alloy capping layer. The simplicity and effectiveness of such a direct solid phase photoresist to graphene conversion method demonstrate its applicability in future mass production of graphene and potential for practical device fabrication in industry.

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Data availability

The datasets generated during and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest

The authors have no relevant conflict of interests to disclose.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1557/s43579-022-00308-z>.

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