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ARTICLE

The growth behavior of graphene on iron-trichloride-solution-soaked copper substrates in a low pressure chemical vapor deposition†

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The copper substrate soaking-treatment of FeCl₃ solution is introduced to reduce the initial nucleation density of graphene significantly (up to 6-fold from 0.29 to 0.05 μm⁻²), where the overall graphene coverage increase-rate is successfully boosted up. The reduction in nucleation density is attributed to the oxidization of copper by treatment of FeCl₃ solution according to the X-ray photoelectron spectroscopy results. The soaking-treatment results in a rougher surface and consequently a significant surface morphology rebuilding during the chemical vapor deposition. Pretreatment of copper substrate with soaking of FeCl₃ solution is a simple and economical approach to control graphene growth. Uttermost, the technique is compatible with the common pattern technique of graphene.

Introduction

Graphene has great application potentials as building block of integrated circuits^{1, 2} and as transparent conductor in flexible electronic devices or energy harvesting components³⁻⁵. It is notable that the two applications possess distinctive requirements upon graphene synthesis technique. Integrated circuits highly require graphene of wafer scale with single domain and there is a great progress in a most recent report⁶. On the contrary, the application of transparent conductor could accept the trade-off of large crystal size graphene with limited numbers of domain boundaries for cost effectiveness. Among the various graphene synthesis methods, chemical vapor deposition (CVD) on copper substrate is the most promising combination for the application of transparent conductor due to capability of mass production in a cost effective way with good quality⁷⁻¹¹. Owing to/benefiting from the industry eagerness for pursuing ultra large size single crystal graphene, CVD on copper substrate method also experiences rapid development where single crystal graphene of centimeter range is achieved¹²⁻¹⁶.

It is worthy to address that reduction in nucleation density during CVD process is the key to achieve graphene of large domain size and high quality. Therefore, efforts have been emphasized on process details (CVD) in suppression of nucleation. For instance, to reduce the hydrocarbon flow or to increase the growth temperature is effective ways to suppress the nucleation. However, a reduction in nucleation density is often associated with price of prolonged growth time for achieving a full coverage. Recently, Hao et al. discovered that control of surface oxygen is another facile approach to suppress nucleation¹⁷. Oxygen exposure during growth enables the growth of large, high electrical quality and single domain

graphene of centimeter in size with hexagon in shape. Unfavourably, the coverage increase-rate is significantly reduced despite of a higher individual domain growth rate.

To smooth the copper surface is another way of reducing the nucleation density. Electropolishing is widely adapted to smoothen and clean the surface for improving the quality of grown graphene^{15, 18}. However, Ivan et al. reported that the quality of graphene on FeCl₃ pretreated copper substrate was as good as those on electropolished copper substrate despite a greater roughness was observed¹⁹. This result was mainly attributed to copper surface rebuilding during the CVD process. In this report, we intentionally studied the dual role of FeCl₃ as both etching and oxidation agent for the copper substrate. As a special experiment design, we divide the growth process into two steps: step1 with high carbon source flow for a short period and step2 with much lower carbon source flow for different period. Such a growth processing allows us to grasp the feature of the graphene growth behaviour as well as the surface morphology changing at both the nucleation stage and the growing stage. An interesting result is that the coverage increase-rate is boost up at a significantly reduced nucleation density.

Experimental

Experiment design and details

The CVD growth of graphene was performed in a 1 inch diameter quartz tube furnace. The copper foil substrates (Alfa Aesar, #13382, 99.8%) were firstly cleaned by acetone, isopropyl alcohol (IPA), ethanol and deionized (DI) water. The FeCl₃ solution treatment of the substrate is depicted in Fig. 1a. The concentration of FeCl₃ solution was 10 mM. Two drops of the FeCl₃ solution were dropped onto a 1 cm² copper substrate

and dried out in the atmosphere. Then both the FeCl_3 -solution-soaked substrate and a not soaked substrate were loaded into the quartz tube furnace for the CVD growth. The CVD parameters are illustrated in Fig 1b. A 40 sccm H_2 flow was kept all through the CVD process. The furnace was firstly heated up to 1000 °C within 40 minutes and then held at this temperature for 20 minutes to anneal the substrate. To highlight the evolution of graphene domains on copper substrate during CVD process, the introduction of CH_4 was divided into two steps: a short period of relatively high flow of CH_4 (step1: 1 sccm for 15 seconds) followed by significantly reduced flow of CH_4 (step2: 0.1 sccm for a period of 15 seconds, 5 minutes and 30 minutes for three experiments, respectively).

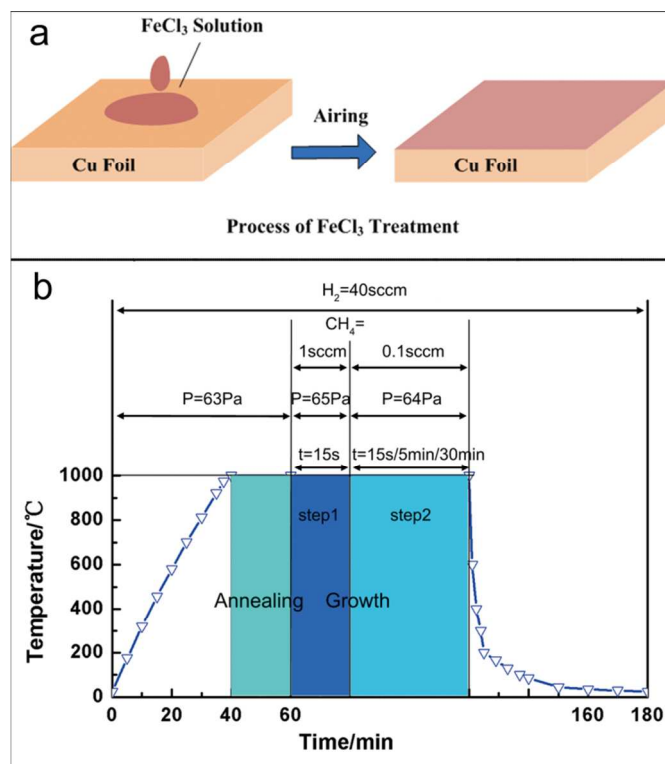


Fig. 1 Illustration of (a) FeCl_3 -solution soaking procedure and (b) the CVD processing flow chart.

Characterization

The surface morphology of the samples was observed by a scanning electronic microscope (SEM, JSM-7000F) operating at 15 kV and an atomic force microscopy (AFM, Innova, Veeco Instruments Inc.). The Raman spectra were recorded by Raman apparatus (HR 800, Jobin Yvon Horiba) with excitation by a laser operating at a wavelength of 514.53 nm. Three-dimension (3D) optical microscopy images were taken by OLS 4000 (Olympus Corporation). X-ray photoelectron spectroscopy (XPS) results were recorded by AXIS ULTRA.

Results and discussion

The SEM images of graphene are shown in Fig. 2. The domains of graphene grown on the FeCl_3 treated substrate ($\text{Graphene}_{\text{treated}}$) are significantly larger compared with the domains of graphene grown on untreated substrate

($\text{Graphene}_{\text{untreated}}$). The domains of $\text{Graphene}_{\text{untreated}}$ are compact in shape, whereas $\text{Graphene}_{\text{treated}}$ is dendritic. As the time span of step2 (t_{step2}) is limited to 15 seconds, the domains of $\text{Graphene}_{\text{treated}}$ are too small/tiny to observe branch shapes (Fig. 2d). But when t_{step2} was further increased to 5 minutes, the domains evolved into six-branched shapes as clearly shown in Fig. 2e. Interestingly, when t_{step2} was further elongated to 30 minutes, most of the six-branched graphene domains immersed to form large domains and lost the clear six-branched shapes (Fig. 2f).

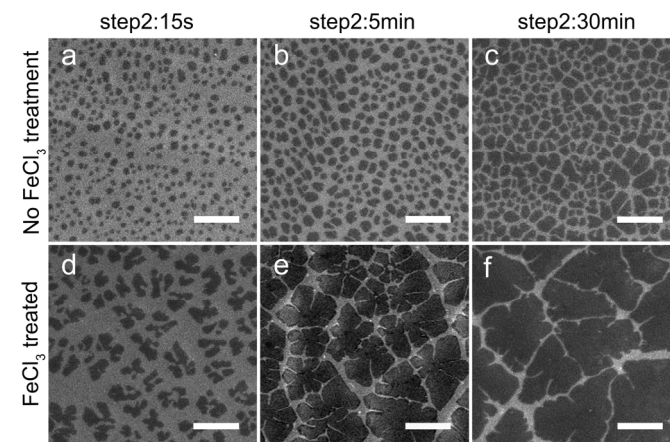


Fig. 2 SEM images (a, b, c) Graphene untreated and (d, e, f) Graphene treated with different t_{step2} . The scale bars in all images are 10 μm .

The asymmetrical six-branched domains in Fig. 2e reveal the intense growth competition between domains. Fig. 3a shows a graphene domain of six highly nonuniform branches, where two individual branches are denoted as A and B respectively. Branch A is significantly sharper at the apex and larger than branch B. There is a void free of domain on the top-right corner of branch A while branch B is closely fronting another domain. The uncovered copper surface on the top-right corner of branch A would enable a faster growth. However, for branch B, the edge would soon approach the nearby domain. The growth at the apex will be suppressed and consequently, resulting in a flattened front edge. Fig. 3b, c illustrates the isotropy of the growth speed in different directions following the method of reference²⁰.

The statistical results of nucleation densities as function of t_{step2} are plotted in Fig. 3d. When t_{step2} is 15s, the nucleation density of $\text{Graphene}_{\text{untreated}}$ is 0.29 μm^{-2} , while that of $\text{Graphene}_{\text{treated}}$ is only 0.05 μm^{-2} . As t_{step2} further increases, both domain densities of $\text{Graphene}_{\text{untreated}}$ and $\text{Graphene}_{\text{treated}}$ drop significantly. For instance, when t_{step2} was 30 min, the domain densities of the $\text{Graphene}_{\text{untreated}}$ and $\text{Graphene}_{\text{treated}}$ dropped to 0.14 and 0.015 μm^{-2} respectively. This result indicates that most of the graphene domains nucleate in step1. Whereas in step2, the significantly reduced flow of CH_4 gives almost no chance to nucleating. As the graphene domains continue to grow larger in step2, they merged with each other and result in a decrease in density of graphene domains.

The graphene coverage on the copper surface is obtained by counting area of graphene domains. The results are shown in Fig. 3e. The counting method is given in the supporting information (Fig. S1). When t_{step2} is 15s, the graphene coverage

ratios of Graphene_{untreated} and Graphene_{treated} are similar, 28% and 30% respectively.

When t_{step2} elongated to 5 min, the coverage ratio of Graphene_{untreated} increased to about 48%, while that of Graphene_{treated} increased to nearly 80%. It is worth noting that the nucleation density of Graphene_{treated} is almost six-fold less than that of Graphene_{untreated}, which indicates a much faster radial growth rate of the domains of Graphene_{treated}. The graphene coverage increase rate is determined by both the nucleation density and radial growth rate of graphene domain. Therefore, it is estimated that the average radial growth rate of domains of Graphene_{treated} is about 3 times larger than that of Graphene_{untreated}. The expression of the coverage increase rate is given by a simple equation S1 in supporting information.

When t_{step2} further elongated to 30 minutes, the coverage ratio of Graphene_{untreated} increased to about 68%. However, that of the Graphene_{treated} only increased by 3% to 83%. It is obvious that the graphene coverage increase slows down at high graphene coverage due to reduction of the copper surface that provides active carbon species. This is a gap-filling stage for the graphene growth. The gaps between the branches were partially filled and graphene domains started to immerge to become larger domains. The healing of the interbranch boundaries has been observed also in our previous work²¹.

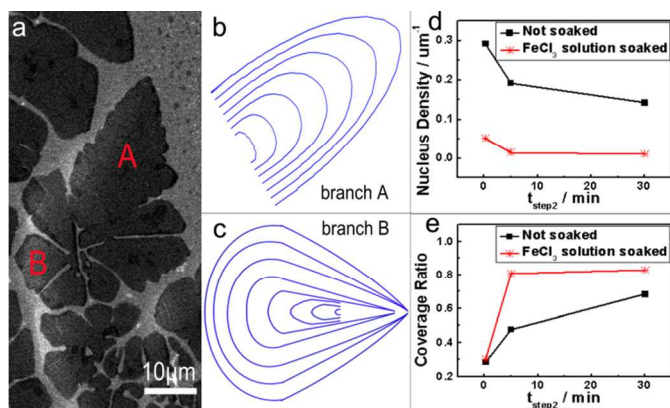


Fig. 3 The graphene growth behaviors. (a) A graphene domain on treated copper foil with six highly nonuniform branches. A and B denote two branches with different size. (b, c) Illustrations of the shape evolution of branch A and B. The statistical results of (d) the nucleation density and (e) the coverage ratio of graphene.

The FeCl₃ aqueous solution treatment could possibly modify the copper surface in two ways: morphology modification and/or chemical modification. The AFM results of treated (Copper_{treated}) and untreated copper (Copper_{untreated}) substrates after high temperature annealing are shown in Fig. 4a, b. The surface of Copper_{untreated} is rather flat with milling trails. However, the milling trails are replaced by random bumpy structures for Copper_{treated}. Much more atomic steps are visible on Copper_{treated}. According to literature²², copper with rougher surface and steps usually provide effective nucleation sites. It is contradictory to our findings. One of the possible reasons is that a rougher surface is more susceptible to contamination, which further improves the nucleation chance. While a rougher surface freshly etched as in our case may don't have that much advantage in nucleation. We believe that the main reason should be attributed to the surface oxidation.

The 3D optical microscopy images of the samples after growth are shown in Fig. 4c, d. The surface of Copper_{untreated} after graphene growth remains flat except for milling trails and few copper hills, which are usually generated by copper sublimation during graphene growth. Strikingly, the random bumpy structures on the surface of Copper_{treated} are replaced by regular copper hills beneath the dendritic graphene domains. The shape of the copper hills is identical to the branched shape of graphene domains. The obtained results indicate significant morphology rebuilding process for Copper_{treated} during graphene growth. The increased roughness on the surface may assist the copper sublimation.

Copper_{treated} was treated with 10mM of FeCl₃ aqueous solution where 1 cm² of copper substrate was subjected to 0.1 ml FeCl₃ aqueous solution. In assuming no lost during CVD process, Fe and Cl atoms should be detectable on surface by XPS. However, signal of Fe atom is covered by background signal and Cl atom is below detection limits. Again, the obtained result is significantly different from reported work¹⁹. The differences may be attributed to the low pressure CVD condition and low concentration of FeCl₃ aqueous solution in our work. The findings suggest that Fe or Cl atoms may not play an important role in changing the graphene growth behavior.

From XPS, Copper_{treated} has a highly enhanced oxygen peak. It is wise to postulate that the Fe³⁺ in aqueous solution, an effective oxidizing agent partially oxidized the surface of copper (Cu) into Cu²⁺ or Cu⁺. As the solution dried out, oxygen impurities would be left on the copper surface.

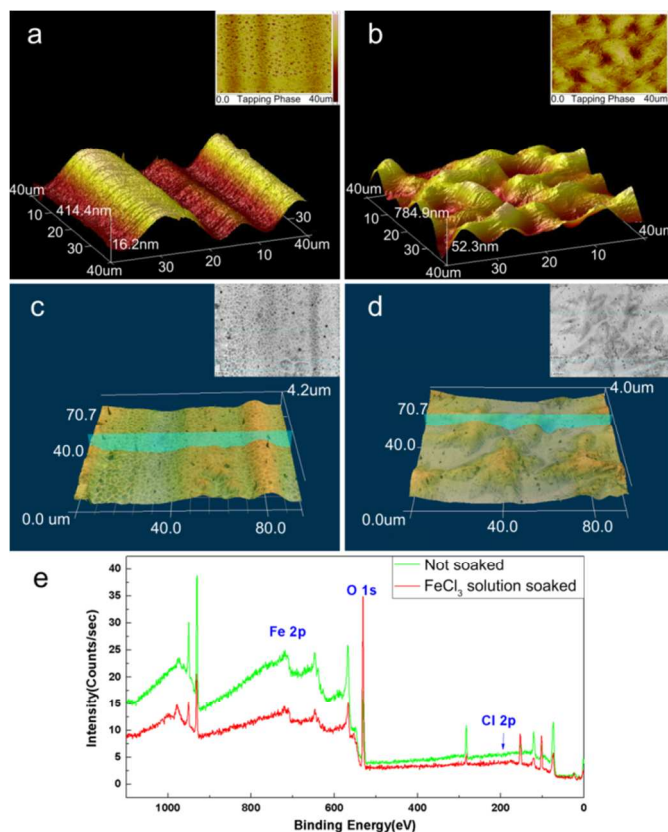


Fig. 4 AFM images of (a) Copper_{untreated} and (b) Copper_{treated}. 3D optical microscopy of graphene grown on (c) Copper_{untreated} and (d) Copper_{treated}. (e) The XPS results of Copper_{untreated} and Copper_{treated}.

The role of oxygen impurities in graphene growth has been fully explored recently¹⁷. It has been proven that oxygen on the surface will significantly reduce the nucleation density. The oxygen on surface also tends to shift the growth kinetic from edge-attachment-limited to diffusion-limited and result in dendritic graphene domains. This is in consistent with our observation for graphene growth on Copper_{treated}. The graphene nucleation on a preoxidized and a 0.5 M FeCl₃ treated Cu substrate are shown in Fig. S2. The nucleation density on both samples decreased significantly.

To further explore the effect of FeCl₃ solution treatment on the growth kinetics, Copper_{untreated} and Copper_{treated} were made into envelopes. Limited to extremely low partial pressure of CH₄ inside envelopes, the density of graphene nuclei is very low and the size of domains reaches about 100 microns (Fig. S3). Under extremely low partial pressure of CH₄ condition, the growth kinetics is diffusion-limited for both Copper_{untreated} and Copper_{treated}. Therefore, the graphene domains for Copper_{untreated} and Copper_{treated} inside envelopes are dendritic with six-branched shape. It is notable that the domains for Copper_{treated} are more dendritic compared with Copper_{untreated}. The result is consistent with effect of oxygen impurities. We believe that oxidization is the main reason of FeCl₃ solution soaking/treatment procedure in changing the graphene growth behavior.

In comparison with O₂ exposure at high temperature, FeCl₃ solution soaking/treatment is a facile room temperature pre-CVD treatment. Oxygen impurities could be selectively introduced to copper surface conveniently via pattern technique. The FeCl₃ solution soaking/treatment reduced the density of nuclei by 6 times, nearly 2 orders higher than the high temperate O₂ exposure technique¹⁷. We have achieved an increase in overall coverage increase rate by moderate reduction in density of nuclei.

The quality of graphene was examined by Raman spectroscopy and transmission electron microscopy (TEM). Fig. 5a is the Raman spectra of graphene grown on Copper_{untreated} and Copper_{treated}. The microscopy images of the samples are shown as inset figures. The sampling spots are denoted by A and B. D peak is not observable in either spectrum. The I_{2D}/I_G intensity ratios are 1.8 and 2.5 for A and B, respectively. The full width at half maximum (FWHM) of 2D band is 26.3 and 31.6 cm⁻¹ for A and B, respectively. Both spectra show a typical feature of a single-layer graphene. A Raman mapping result of a six-branched graphene domain grown in a copper foil envelop is shown in Fig. S4. It is confirmed that the branched graphene domains are single layer. The high resolution TEM image of the graphene which was prepared on Copper_{treated} is shown in Fig. 5b. And the corresponding diffraction pattern is showed as Fig. 5c. Both of them confirm a perfect honeycomb lattice of graphene domain grown on Copper_{treated}. The Raman results and TEM analysis indicate that the FeCl₃ solution soaking/treatment procedure does not result in observable quality degradation of graphene growth.

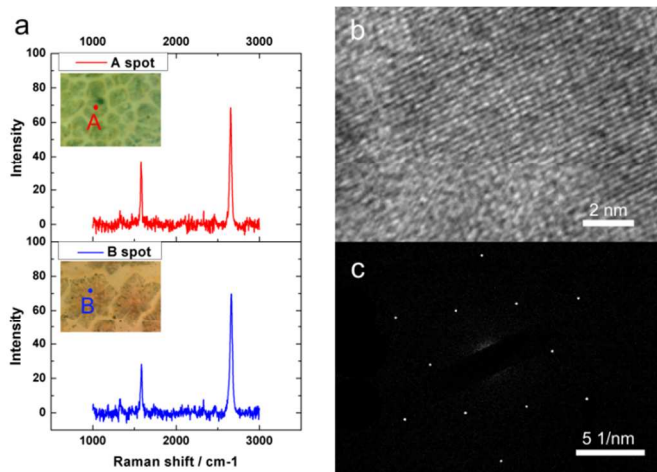


Fig. 5 (a) The Raman spectra of Graphene_{untreated} (red spectrum) and Graphene_{treated} (blue spectrum). The inset optical microscopy images show the sampling spots. (b) A high resolution TEM image of a graphene domain on Copper_{treated} and (c) its corresponding diffraction pattern.

Conclusions

FeCl₃ solution soaking was adopted as a Cu substrate treatment prior to the CVD process. The graphene nucleation density was reduced by nearly 6-fold, while the total graphene coverage increase-rate was boosted up with FeCl₃ solution soaking procedure. The graphene domains tend to be more dendritic on Copper treated. Dense six-branched graphene domains on Copper treated was observed. The rougher surface of Copper treated denies the possibility of the morphology modification playing the main role in changing the growth behavior. The XPS results revealed significantly increased oxygen impurities on Copper treated. The FeCl₃ solution soaking of the Cu substrate makes the graphene domain more dendritic. The reduced nucleation density and the highly dendritic feature of the graphene domains on Copper_{treated} are attributed to the increased oxygen impurities. The Raman spectra and TEM results confirmed that the FeCl₃ solution soaking procedure didn't cause observable graphene quality degradation.

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Notes and references

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