On the Dynamics of Intrinsic Carbon in Copper during the Annealing Phase of Chemical Vapor Deposition Growth of Graphene

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ABSTRACT: In chemical vapor deposition (CVD) growth of graphene, intrinsic carbon in copper has been shown to play a role, especially during the nucleation phase. Here, we report experimental results on depletion of carbon from the bulk of a Cu foil to its surface at different hydrogen pressures, which explain new aspects of the interplay between hydrogen and intrinsic carbon prior to growth. We observed that rising H2 pressure boosts carbon depletion to the surface, but at the same time, at elevated H2 pressures, the graphitic film formed on the Cu surface is etched away at a faster rate. This effect led us to practice annealing of copper under high hydrogen pressure as an approach to decrease the total content of carbon in the copper foil and consequently reducing the nucleation density of graphene flakes. These results enhance our understanding about the role of H2 in the CVD process and explain some of the inconsistencies among the earlier reports.

1. INTRODUCTION

Since the first report of the synthesis of a graphene film on a copper foil using chemical vapor deposition (CVD), significant progress in different aspects of this technique has been achieved and it has become the most promising method for producing graphene for various applications. The demand for an economical and reproducible recipe for graphene production has progressively expanded the research for understanding the mechanisms during the growth of graphene in the CVD process. It has been considered that the very low solubility of carbon in copper makes the graphene growth process primarily governed by surface-adsorption and inherently self-limited. A weak surface diffusion barrier for carbon ad-atoms leading to high mobility of carbon on copper at high temperatures is another reason for the growth of graphene to be considered as a pure surface-based process. Briefly, CVD growth of graphene is described to be initiated with the adsorption of carbon precursor molecules on copper surface, followed by their dissociation to form active carbon species which diffuse on the surface until trapped and accumulated at defect sites. Increase in the carbon concentration at defect sites leads to supersaturation of carbon and finally the nucleation of graphene flakes (GFs).

During the CVD synthesis of graphene, where just a few atoms can have a substantial effect on the growth of one-atom-thick carbon crystals, slight variations in conditions may substantially alter the delicate processes at high temperatures and can easily lead to irreproducibility. This instigates significant difficulties against uncovering the underlying mechanisms of the growth of graphene on copper. For example, passivation of nucleation sites due to reaction with oxygen was initially suggested as the reason for the suppression of graphene nucleation in the presence of diluted oxygen. However, later it has been agreed that the reduction in the nucleation is mainly due to the etching of carbon from the surface of the Cu foil by oxygen. Likewise, whereas most of the studies on nucleation and growth of GFs were focused on the role of an external carbon source, either in the form of precursor or contamination, only very recently has the role of carbon inside the foil in the nucleation of GFs been revealed.

As Cu foil has been widely considered to behave as pure copper with very low solubility for carbon, the intrinsic carbon incorporated in the Cu foil during its production has been overlooked for many years. However, a few recent reports imply that the presence, dissolution, and diffusion of carbon inside the copper foil makes the nucleation and growth of graphene to be more complex and a multifunctional process than what was proposed earlier. Therefore, to achieve a comprehensive model for the nucleation of GFs on the Cu foil, it is essential to understand the interplay between “presence, dissolution, and diffusion of carbon inside the copper foil” and other parameters such as concentrations of oxygen and hydrogen.

Depending on its concentration, oxygen has different effects on carbon in the Cu foil either as an etchant or as a scavenger of carbon from the foil or as an impurity, which raises the solubility/diffusivity of carbon inside the Cu foil. Although the etching effect of hydrogen has initially been

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reported, \(^{36-40}\) later it has been argued that oxygen/water from hydrolyzers caused the etching of carbon on the surface of Cu, which led to discrepancies among the reports about the nucleation process. \(^{41,42}\) However, the effect of hydrogen on the carbon inside the bulk of the Cu foil has not yet been fully described for the CVD process.

In a previous work, we demonstrated spontaneous nucleation of graphene on copper during the annealing stage under hydrogen in the absence of any external carbon precursor. Our results not only confirmed that the initially nucleated GFs on the Cu foil could be directly fed by out-diffusing intrinsic carbon from inside the foil as a spontaneous effect, but also disclosed the key role of hydrogen on depletion of carbon from the bulk of the Cu foil to its surface as hydrogen-assisted carbon depletion (HACD). \(^{34}\) We have also observed that the H\(_2\) partial pressure during the annealing of the Cu foil has a major effect on the structure of the carbon film; at H\(_2\) pressures as low as 1.4 mbar, spontaneous nucleation of graphene is favored, but when the pressure was increased to 6 mbar predominantly disordered graphitic film (DGF) formation has occurred on the surface. \(^{33}\)

However, the effect of extending H\(_2\) to a higher level in our recent experiments ended up with etching of carbon from the copper surface, and suppressing or even terminating the spontaneous nucleation of graphene on copper. These results elucidate further details about the role of hydrogen in the CVD process for growth of graphene on Cu foil and can explain part of the inconsistencies among some earlier reports. \(^{4,34,35,39-41,42}\) Supported by time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth-profile measurements of carbon in Cu foil together with optical microscopy and scanning electron microscopy (SEM) characterizations of the annealed surfaces, we revealed two simultaneously acting processes under a high concentration of hydrogen, accumulation and etching of a carbon film on the Cu surface.

2. RESULTS AND DISCUSSION

In the experiments reported here, we observed that depending on the H\(_2\) concentration, the annealing process can result in formation of either DGF or graphene with varying coverages and qualities, or a completely carbon-free surface. In all cases, migration of carbon from the bulk to the surface was evident from the ToF-SIMS depth-profile measurements of carbon in annealed Cu foil samples which is consistent with the HACD mechanism. We also discovered that, another mechanism removes carbon from the Cu surface very efficiently in the presence of high H\(_2\) concentrations; both growth and etching of DGF takes place simultaneously and an intricate balance between these processes results in either spontaneously nucleated GFs (SNGFs), DGFs, or bare Cu surfaces for low, medium, or high concentrations of H\(_2\), respectively.

Finally, we practiced annealing of copper under maximized hydrogen pressure for the purpose of reducing the carbon content in its bulk and consequently achieved a reduction in the density of SNGFs. To obtain compatible data with our earlier report, \(^{34}\) we used the same setup, materials, and procedures in the experimental methods presented here. The details are given in the Experimental Methods section.

2.1. Etching of Carbon under a High Concentration of Hydrogen. To investigate the effect of H\(_2\) partial pressure on intrinsic carbon during annealing, Cu foil samples (99.8% metallic pure) were annealed under H\(_2\)/Ar atmosphere with varying pressures and concentrations of H\(_2\). The details of the annealing parameters are given in Table 1. In Figure 1, SEM images of these samples after annealing are demonstrated for comparison. P-x denotes a sample annealed under H\(_2\) partial pressure of x mbar. One naively expects to observe an increasing accumulation of DGF as the sample index runs from P-6 to P-17 and then to P-60, simply because of boosting of HACD. However, as it can be seen in the SEM images in Figure 1, whereas the P-6 surface was fully covered by DGF, in P-17 the DGF was partially etched, and in P-60 DGF had

| sample | annealing time (min) | H\(_2\)/Ar flow rate (sccm) | process pressure (mbar) | H\(_2\) pressure (mbar) | figure | DGF coverage |
|--------|----------------------|-----------------------------|-------------------------|------------------------|--------|--------------|
| P-6    | 20                   | 200:500                     | 20                      | 6                      | Figures 1 and 2 | full         |
| P-17   | 20                   | 200:500                     | 60                      | 17                     | Figures 1 and 2 | partial      |
| P-60   | 20                   | 200:0                        | 60                      | 60                     | Figures 1 and 2 | none         |

“After annealing under 6 mbar H\(_2\) partial pressure without using any external carbon precursor, DGF is formed on the surface of Cu foils. DGF coverage is determined by scanning electron microscopy and also verified by ambient oxidation. However, increasing the H\(_2\) pressure resulted in partial or full etching of the graphitic layer on the copper surface.”
or above H2 pressure. Accordingly, the crossing of carbon near the surface is decreased after annealing at 17 mbar.

SEM and optical microscopy images (Figures 1 and 2) and the DGF (Figure 2) demonstrate enhancement of carbon depletion and the samples annealed in 6 mbar (P-6), 17 mbar (P-17), and 60 mbar (untreated, P-6, P-17, and P-60). The comparison of untreated Cu copper foils treated in different levels of hydrogen pressure (untreated, P-6, P-17, and P-60) were demonstrated in the literature.4,39-44 Depending on the relative rate of these counteracting mechanisms, either the growth or the etching of the graphitic film on the copper surface dominates at different stages of the thermal treatment.45

Here, we discuss three possible mechanisms that can cause or enhance the etching of the graphitic layer when hydrogen is introduced during annealing:

(i) Etching by oxidative impurities in hydrogen gas: role of oxygen and/or oxidative impurities in H2 gas (even at the ppm level concentrations) on etching of graphene were demonstrated in the literature.4,41,42 The pressure of H2 also determines the partial pressures of its oxidative impurities and therefore the etch rate should depend on the pressure, as well. We used 99.999% pure gases with a constant flow rate in each of our experiments. However, as the carbon content in the copper foil is finite, the rate of out-diffusion of carbon declines in time during the annealing and at a certain point etch rate exceeds the growth rate.

(ii) Enhanced etch rate of DGF because of inherent defects: here, we can consider two extreme conditions. On one side, applying very low hydrogen pressure reduces the density of SNGFs due to reduction of the HACD mechanism and hence the reduced number of supersaturated spots on the surface. In this scenario, because of the minimized density of SNGFs, larger size GFs with lesser edge atoms and lesser defects per area will grow on the surface. On the other side, applying high hydrogen pressure causes a fast carbon depletion and generates supersaturation at numerous points on the surface of the copper foil. However, the high density of supersaturated sites on the surface will result in a DGF with very small size graphitic domains and with more defects and edges.46 A more defected graphitic film is more prone to chemical etching described in (i). Therefore, whereas the rate of out-diffusing carbon declines during annealing, the etch rate exceeds the growth rate and dominates during the early stages. As a result, more defected DGF is etched faster; this is consistent with the observations of partially etched P-17 and fully etched P-60.

(iii) Etching assisted/cause by hydrogen: although it has been discussed that unintentional oxidative impurities...
cause the etching effect on graphene in hydrogen atmosphere as in HACD different mechanisms for spontaneous nucleation of graphene or growing DGF are taking place, the possibility of etching by hydrogen needs to be taken into account. Higher H$_2$ concentration enhances the chance of reaction of C radicals with H$^+$ ions over the surface of copper and formation of C–H bonds instead of the C–C bonds. Addition of these defect sites in DGF increases the etch rate of the film by oxidative gas impurities. Therefore, an increased concentration of H$_2$ applied during the processing of P-17, compared to P-6, may have induced more defects and speeded up the etching mechanisms described in (i) and (ii). Under even higher hydrogen concentration, H$^+$ ions can totally passivate the carbon radicals that arrive at the surface and form volatile C$_x$H$_y$ molecules which eventually evaporate at 1000 °C. Therefore, a graphitic film could not grow on P-60.

2.2. HACD as a Pretreatment To Suppress Graphene Nucleation. Different aspects and varying effects of HACD on the Cu foil under different H$_2$ concentrations is summarized in the schematic diagram demonstrated in Figure 4. As the H$_2$ partial pressure is increased, the migration of carbon to the surface is enhanced because of HACD. At sufficiently high pressure, the rate of removal of carbon from the surface surpasses its rate of accumulation on the surface, resulting in a nearly carbon-free bulk and surface. In this section, we utilized HACD to effectively deplete the intrinsic carbon in a Cu foil as a pretreatment to suppress spontaneous nucleation of graphene. Sample P-1.4, which is used as reference, was annealed under 1.4 mbar H$_2$ and dense SNGFs were observed on its surface. Sample P-1.4D had undergone the pretreatment of annealing under 60 mbar of H$_2$ followed by a second annealing phase, which is the same as applied on sample P-1.4 (in favor of spontaneous nucleation of graphene from the remaining carbon rather than etching them from the surface). Process details for these experiments are given in Table 2 and the SEM images of samples P-1.4 and P-1.4D are illustrated and compared in Figure 5. Carbon depletion in the first phase of annealing of P-1.4D resulted in 95% reduction in the density of SNGFs compared to P-1.4. These results demonstrate the correlation of density of the nucleation sites with the density of intrinsic carbon in the Cu foil. H$_2$ pretreatment was reported in earlier reports; nevertheless, hydrogen “surface” cleaning was proposed as the mechanism for the observed reduction in the nucleation density.

We measured and compared the carbon depth profiles of P-1.4 and P-1.4D by ToF-SIMS to verify the connection between reduction in the density of SNGFs and density of intrinsic carbon. The carbon depth profiles of an untreated sample and P-1.4, and P-60 and P-1.4D are given in Figure 6. We observe a similar trend in changing of the carbon profile from untreated to P-1.4 and from P-60 to P-1.4D but with an overall reduced intensity in the latter. In both cases residual carbon migrates and accumulates toward the copper surface when annealed under 1.4 mbar H$_2$ pressure. Overall, the carbon profile in P-60 was reduced by about 1 order of magnitude compared to the untreated sample, which means that there is an order of magnitude lesser carbon near the surface of P-1.4D after its pretreatment at 60 mbar H$_2$ compared to P-1.4 (inset of Figure 6). This explains why the nucleation density of GFs in P-1.4D is about 1 order of magnitude lesser than that of P-1.4, as given in Table 2 and displayed in Figure 5.

Here, we need to mention that the P-1.4D profile has a different curve shape, exhibiting a shoulder near the surface. This is due to the increased size of GFs on P-1.4D. Larger GFs block the normal to the surface diffusion pathways for both hydrogen from outside into the copper bulk and for carbon from inside of copper to its surface. Therefore, as the HACD process slows down in the proximity of GFs, the slope of the carbon profile declines near the P-1.4D surface.

Additionally, as can be seen in Figure 5, coverage and average flake size on P-1.4D is more than on P-1.4 even though P-1.4D has lesser carbon than P-1.4 (35% coverage and 1 μm$^2$ flake size for P-1.4, and 50% coverage and 20 μm$^2$ flake size for P-1.4D). The increased size and coverage in P-1.4D is because graphene growth is not a linear mechanism and has a faster rate when there is a larger distance between neighboring flakes.

3. CONCLUSIONS

Here, we reveal novel results about the effect of H$_2$ pressure on the dynamics of intrinsic carbon in a Cu foil during annealing. On the basis of our earlier report, because of accumulation of carbon from the bulk onto the Cu surface via HACD, a spontaneous nucleation of graphene or growth of GFs/graphitic film is expected. However, we find that at high pressures of H$_2$ the Cu surface becomes free from the carbon film. These results are interpreted in terms of two effects ongoing simultaneously, accumulation of carbon and its etching from the surface.
Table 2. Annealing Parameters and the Calculated Density for the Samples P-1.4 and P-1.4D*

| sample   | initial annealing (40 min) | second annealing (40 min) |
|----------|----------------------------|----------------------------|
|          | H₂/Ar flow rate (sccm)     | process pressure (mbar)    | H₂ pressure (mbar) | graphene nucleation density (mm⁻²) |
| P-1.4    | 50:500                     | 16                         | 1.4                | 6 x 10⁵                         |
| P-1.4D   | 50:500                     | 16                         | 1.4                | 2.3 x 10⁴                      |

*Sample P-1.4D was initially treated before applying on it the same annealing process as P-1.4. The initial treatment for P-1.4D was the depletion of the carbon in the bulk by the application of the same procedure as P-60. Nucleation density is dramatically reduced in this sample.

Increasing the hydrogen pressure boosts the HACD mechanism, which leads to supersaturation of the whole copper surface, resulting in a defected DGF. Further increase in H₂ pressure causes rapid formation of a DGF which is fragile against etching and is completely removed from the surface by the end of the annealing phase. We discussed that the higher H₂ pressure causes more defects in the graphitic structure grown on the Cu foil. As a result, the presence of oxidative impurities in the flowing gas can be more effective on etching of the more defected DGF.

Furthermore, we used the boosted HACD at maximized H₂ pressure of the system as a pretreatment approach to effectively reduce the carbon content of the Cu foil and minimize SNGFs in another step of annealing at 1.4 mbar H₂. Carbon profile measurements correlate reduction in density of SNGFs and the depletion of intrinsic carbon.

4. EXPERIMENTAL METHODS

In this work, a CVD furnace with an 11 cm inner diameter of the quartz tube has been used. Details of the setup can be found in ref 34. 2 x 3 cm² sized Cu foils (25 μm-thick, <0.2 μm roughness, 99.8% metallic pure LiB grade, P.N. B1-SBS, purchased from Taiwan Copper Foil Co. LTD.) were used for each annealing experiment. To remove ambient gas from the system, the CVD system has been pumped down and then flushed with argon several times. Then, at the base pressure of 5 x 10⁻² mbar, the system was heated up from room temperature to 1000 °C in 40 min, followed by the annealing phase at 1000 °C. During the whole duration of thermal treatment of copper, only hydrogen (99.999% pure) and argon (99.999% pure) were flowing in the system. To exclude carbon contamination from the pump oil, a dry pump (Agilent TriScroll 300) has been used to pump the chamber and to exclude cross-contamination from an external carbon precursor, new quartz tubes were used in this work that have never been used for growth experiments.

To characterize the surface of Cu samples after the thermal treatment, we used optical microscopy and SEM (Zeiss Gemini 1530). Then, to measure the depth profile of the carbon inside the Cu foils, ToF-SIMS technique has been implemented (TOF SIMS S, ION-TOF GmbH). For the sputtering cycle, we used 2 keV Cs⁺ ions with 70 nA current and a 25 keV, 1.5 pA Bi³⁺ ion beam is used to do SIMS measurement after each sputtering cycle. The cycle time of the Bi³⁺ ion current was 100 μs in the interlaced mode. To avoid the generated spectra from the edges, the SIMS signal acquired from 150 x 150 μm² co-centered with a 400 x 400 μm² sputtered region is recorded. The signals detected from the top 1.9 nm of the Cu foils were excluded from the measurement to avoid the portion of adsorbed organic molecules from ambient air. The local minimum of the CH⁺ ions’ intensity during depth-profiling determines the depth of exclusion, 1.9 nm.

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Notes
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