Spontaneous Nucleation and Growth of Graphene Flakes on Copper Foil in the Absence of External Carbon Precursor in Chemical Vapor Deposition

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ABSTRACT: In this work, we uncover a mechanism initiating spontaneous nucleation of graphene flakes on copper foil during the annealing phase of chemical vapor deposition (CVD) process. We demonstrate that the carbon in the bulk of copper foil is the source of nucleation. Although carbon solubility in a pure copper bulk is very low, excess carbon can be embedded inside the copper foil during the foil production process. Using time-of-flight secondary ion mass spectrometry, we measured the distribution profile of carbon atoms inside the copper foils and its variation by thermal annealing. We also studied the role of hydrogen in the segregation of carbon from the bulk to the surface of copper during annealing by scanning electron microscopy and Raman analysis. We found that carbon atoms diffuse out from the copper foil and accumulate on its surface during annealing in the presence of hydrogen. Consequently, graphene crystals can be nucleated and grown while “any external” carbon precursor was entirely avoided. To our knowledge, this is the first time that such growth has been demonstrated to take place. We believe that this finding brings a new insight into the initial nucleation of graphene in the CVD process and helps to achieve reproducible growth recipes.

1. INTRODUCTION

Since the first demonstration of the growth of graphene by chemical vapor deposition (CVD) on copper,1 a variety of improvements such as achieving centimeter size single crystals2−5 and high carrier mobility comparable to mechanically exfoliated graphene have been realized.6 These developments have made CVD growth on copper the most prominent method for graphene production for various suggested applications.7−9 Therefore, the high demand for an economical and reproducible technique for the mass scale production of high quality graphene has led to many studies on CVD growth mechanisms.10−23 Li et al. demonstrated that due to the very low solubility of carbon in copper, surface-adsorption governs graphene growth and makes it a self-limited process.10 The growth terminates as soon as the copper surface is fully covered with graphene, since the active surface area on which to catalyze methane decomposition and supply the carbon source is lost. It has thus been suggested that besides the very low solubility of carbon in copper bulk, the high mobility of carbon ad-atoms on copper due to the weak surface diffusion barrier can boost the pure surface-based process mechanism.14,24,25

CVD growth of graphene is generally explained to begin with the adsorption of a hydrocarbon molecule on a catalyst surface followed by its dissociation into active carbon radicals that diffuse on the surface until they agglomerate on defects. This local concentration increases until the supersaturation level is reached and crystal nucleation has started on defect points.23

The dramatic suppression of graphene nucleation attained by introducing oxygen to the CVD process has been a critical development towards the growth of high quality graphene.2,26 However, it has taken a while to understand the suppression of nucleation and its relation to the reduction of carbon content in copper foil.19,27,28 Also, recent growth of graphene “with ‘no’ feedstock” but from pump oil highlighted the role of external carbon contamination.29

In this study, we reveal the role of intrinsic carbon diffusing out from the copper foil upon nucleation and growth of graphene crystals when other sources of carbon contamination were meticulously avoided. As a result, for the first time, to our knowledge, we demonstrate the growth of micron-sized graphene flakes (GFs) on copper foil up to the near full surface coverage in the absence of any external carbon source.
To measure the carbon content in the Cu foils, we used a time-of-flight secondary ion mass spectrometry (ToF-SIMS) technique, which has a high mass resolution power ($\approx 10^5$) at a ppm level of elemental detection. We show that before the beginning of the graphene growth phase, hydrogen induces migration of carbon atoms from inside copper foil towards its surface (H-assisted C depletion).

The intensity profile of the carbon content versus depth in Cu foils measured with ToF-SIMS provided not only direct evidence for the presence of intrinsic carbon within the bulk of copper foil, but also confirms the depletion of carbon from the bulk towards the surface of Cu foil assisted by H during annealing.

As it is discussed in detail in Section 3, we observed two possible consequences of hydrogen-induced carbon depletion depending on the hydrogen partial pressure: (i) growth of the disordered graphitic layer on copper; (ii) nucleation and growth of graphene flakes from carbon impurity trapped in the copper bulk. Our experiments indicate that the use of low hydrogen concentration in a CVD process makes the second consequence to be the most likely outcome. This leads to an uncontrolled spontaneous nucleation and growth of graphene flakes (GFs) during the annealing phase, before any carbon precursor is fed into the system. This premature growth leads to an increased density of nucleation sites and, hence, reduces the average crystal size and quality of graphene films.

The systematic work presented in this paper on the H-assisted C depletion mechanism unveils an important detail about the origin of the nucleation of graphene crystals and elucidates the relationship between the nucleation density and process parameters.

2. EXPERIMENTAL SECTION

We used a CVD system with a 11 cm inner diameter quartz tube during the experiments. 25 $\mu$m-thick ultra-smooth Cu foils (<0.2 $\mu$m roughness, 99.8% metallic pure LiB grade, P.N. B1-SBS) purchased from Taiwan copper Foil Co. LTD. were used for main experiments. In addition, 99.999% metallic pure copper foil (25 $\mu$m thick purchased form Alfa Aesar, P.N. 10950) representing different levels of purity was used for comparison. Both types of Cu foils are not oxygen free. For each test, we used a 2 x 3 cm$^2$ sized Cu foil. To provide a uniform gas flow over the foil, it was placed on a 10 cm diameter quartz tube centered inside the main tube. The ambient gas is removed from the CVD system by three times pumping down to $10^{-3}$ mbar followed by flushing with argon to 300 mbar. After this, when the system reached a base pressure of $5 \times 10^{-2}$ mbar the process was initiated by heating the system from room temperature to 1000 °C in 40 min, followed by an annealing phase at 1000 °C. Only hydrogen (99.999% pure) and argon (99.999% pure) were injected into the system during the heating up and annealing phases to treat the copper surface. The pressure of the chamber was tuned by the uniform gas flow rates. The cooling of the chamber from 1000 to 200 °C took 10 min. A set of fresh quartz tubes (inner tube 10 cm and outer tube 11 cm diameter, 99.998% pure, Yukanq Quartz Ltd.) are used for the experiments in this work to exclude cross contamination. Moreover, the tubes were baked at 1000 °C for 2 h under a 500 sccm flow of argon before the experiments.

We used scanning electron microscopy (SEM, Zeiss Gemini 1530) to structurally characterize the copper samples and graphene. A wet transfer process is used to transfer graphitic films and graphene flakes from the copper on to SiO$_2$/Si substrates for Raman characterization. First, a thin layer of poly(methyl methacrylate) (PMMA) (MicroChem 950 PMMA 2% in chlorobenzene) was spin-coated on the samples and baked at 180 °C for 5 min. Then, the unintentionally grown graphene at the back-side of the foil was removed by oxygen plasma. Next, the samples were placed in 0.1 M aqueous ($\text{NH}_4$)$_2\text{S}_2\text{O}_8$, overnight. After the copper foil was etched away, the graphene film with PMMA support was transferred from the solution into deionized (DI) water. Three cycles of 10-min DI water rinsing were applied to wash away the remaining etchant. Then the film was picked up from water on a SiO$_2$/Si substrate. Finally, the PMMA was dissolved using a hot acetone bath at 70 °C, rinsed with 2-propanol and dried with blowing compressed nitrogen. We used Raman spectroscopy (Renishaw inVia Reflex) to confirm the presence of carbon-based layers on the copper samples or after transfer.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to take the depth profile of the carbon content in the Cu foils, using TOF SIMS 5 (ION-TOF GmbH). To avoid edge effects on the generated spectra, SIMS measurement is performed by analyzing a 150 × 150 $\mu$m$^2$ area at the center of a 400 × 400 $\mu$m$^2$ sputtered region. 2 keV Cs$^+$ ions with 70 nA current is used during the sputtering cycle and spectra are obtained by using a 25 keV Bi$^{3+}$ ion beam after each sputtering cycle. The ion current of Bi$^{3+}$ was 1.5 pA in the interlaced mode with a cycle time of 100 μs. We omitted the detected ions from the top 1.9 nm of the samples to exclude the contribution of adsorbed carbon from ambient air. This depth was determined from the local minimum of the CH$^-$ ions signal during depth profiling.

3. RESULTS AND DISCUSSION

Although we meticulously avoided any carbon contamination in our CVD setup, annealing of copper foil under relatively high concentrations of hydrogen ambient led to the formation of graphitic films on its surface. A series of annealing tests and ToF-SIMS depth-profile measurement of carbon in the Cu foils confirmed the presence of intrinsic carbon and its depletion to the surface during hydrogen annealing (H-assisted C depletion). On the other hand, under lower hydrogen pressure, graphene flakes were nucleated and grown without any external carbon precursor. In fact, we realized that due to the depletion of carbon from the bulk to the surface of the copper foil, the formation of nucleation sites on the surface is initiated during the annealing phase before any external carbon precursor is introduced. The details of our results are described in the following subsections.

3.1. Presence of Intrinsic Carbon and Its Depletion. In the first set of experiments, three samples of copper foil were used to investigate the effect of hydrogen partial pressure on the depletion of intrinsic carbon during annealing.

The first two samples were annealed for 20 min under the hydrogen partial pressure values of 0 and 6 mbar and labeled accordingly as P-0 and P-6, respectively. To avoid restructuring the surface of P-0 and forming cuprous oxide (Cu$_2$O) due to oxygen impurities as the temperature descends, P-0 was cooled down under 6 mbar hydrogen.
The details of the annealing conditions are given in Table 1, and Figures 1, S1 and S2 display the SEM images of the corresponding samples after annealing. The annealing of P-0 caused some changes in the morphology of the copper surface such as the enlargement of the copper grains and reduction of the native oxide layer (Figure S4), as expected.30 However, there is another noticeable change in P-6 which is annealed under a hydrogen atmosphere; the emergence of a dark thin film fully covering the surface of P-6 as well as black spots scattered over it as seen in Figures 1b and S2. The surface coverage on P-0 and P-6 were also tested by ambient oxidation31 as explained in detail in the Supporting Information (Figure S5).

Table 1. Annealing Parameters for Samples P-0, P-6, and P-0-6

| sample | annealing time (min) | H2/Ar flow rate (sccm) | process pressure (mbar) | H2 pressure (mbar) | figures | surface |
|--------|----------------------|------------------------|-------------------------|------------------|---------|---------|
| P-0    | 20                   | 000:500                | 15                      | 0                | 1a, S1  | bare    |
| P-6    | 20                   | 200:500                | 21                      | 6                | 1b, S2  | DG film |
| P-0-6  | 0–20 min             | 000:500                | 15                      | 0                | 1c, S3  | bare    |
|        | 20–40 min            | 200:500                | 21                      | 6                |         |         |

“Without using any external carbon precursor, a disordered graphitic (DG) film is formed on the surface of P-6 due to the diminishing oxygen scavenging mechanism using H2 flow from the beginning of annealing.

Figure 1. (a) SEM image of the sample P-0 surface after 20 min annealing under argon flow with no hydrogen. No specific feature can be seen on the P-0 surface except for a few white spots identified as silicon oxide particles. (b) The SEM image of the sample P-6 surface after 20 min annealing under 6 mbar hydrogen pressure. The copper surface is fully covered by a graphitic thin film and darker spots signify denser graphitic features. (c) The SEM image of the sample P-0-6 surface which was first annealed just as P-0 and then as P-6 in the same cycle; its surface shows no carbon features on it. During the first 20 min of annealing without hydrogen, carbon impurities were scavenged by oxygen impurities, thus, during the second 20 min annealing phase under hydrogen no graphitic thin film could be grown due to the absence of carbon supply. Large area SEM images of P-0, P-6, and P-0-6 can be seen in Figures S1–S3, respectively. (d) The Raman spectra of P-0, P-6 before and after its transfer on a SiO2/ Si substrate, and P-0-6. D and G peaks, around 1350 and 1600 cm⁻¹ verify the presence of the disordered graphitic structure on P-6, however, no graphitic peak can be seen in the Raman spectra of P-0 and P-0-6.
performed a control experiment on a third sample (P-0-6), comprising a two-step annealing process as follows: during the first 20 min of annealing, no hydrogen was used as in the case of P-0, then the annealing was continued for another 20 min under 6 mbar hydrogen partial pressure as P-6. The bare surface of P-0-6 at the end of the process as can be seen in Figures 1c, S3 and S5f verifies that the growth is not from carbon contamination, neither in hydrogen gas nor from other external sources. We conclude that the carbon atoms emerged on the P-6 surface originated from the copper foil itself. In the following paragraphs, we explain the microscopic mechanisms leading to the depletion of carbon in P-0 and P-0-6 and carbon film formation on the P-6 surface.

Here, we also need to note that the bare surface of P-0-6 compared to P-6 confirmed the absence of carbon outgassing from the quartz tube, as the same quartz tube has been used for both experiments.

We performed ToF-SIMS experiments to directly verify the existence of intrinsic carbon inside the copper foil and its depletion to the surface during annealing under a hydrogen atmosphere. We determined the carbon concentration profile with respect to the depth from the surface on P-0, P-6, P-0-6 as well as the untreated copper foil (T-0). As it can be seen in the intensity profile of the C$_2$ ion in Figure 2, the carbon concentration in untreated sample T-0 rapidly declines as a function of distance from the surface within a few tens of nanometer depth. This data verifies the carbon content in copper and the profile with increasing concentration towards the surface supports the proposal that carbon is embedded in the Cu foil during the rolling and foil production process. This is somewhat similar to the process of mechanical alloying of carbon and copper. On the other hand, ToF-SIMS measured more than 1 order of magnitude above the background level carbon concentration well below the surface in T-0. The existence of carbon deeper in the foil may be connected with impurities initially existing in the copper material before the foil production process. In the P-0 sample, which was annealed for 20 min without hydrogen, we observe that the carbon profile has undergone a significant change. The carbon level is reduced throughout the measured depth and, in particular, there is 2 orders of magnitude reduction in the carbon level near the surface of P-0 compared to the untreated foil, T-0. In contrast, 20 min annealing of P-6 under 6 mbar hydrogen increased its carbon concentration near the surface. Also, compared to P-0, there is less drop in the carbon level of P-6 below 10 nm. The very similar depth profile of P-0-6 to P-0 implies a similar mechanism for the reduction of its carbon content during its first 20 min annealing step and no effect of hydrogen during its second step of annealing. Such a transformation in the carbon profile demonstrates the total depletion of carbon from copper foil in the absence of hydrogen during annealing but the migration of carbon from the bulk of copper foil towards its surface during annealing in the presence of hydrogen.

Here, we propose a microscopic mechanism that causes the intrinsic carbon to migrate and accumulate on the surface of copper foil in the presence of hydrogen as in the case of sample P-6. At elevated temperatures on the surface of Cu, H$_2$ dissociate to its atoms and dissolve in the copper bulk and releases carbon from Cu–O–Cu bonds and depletes oxygen in the form of H$_2$O vapor. This process reduces the chance of intrinsic oxygen to scavenge the carbon. Reducing oxygen from the Cu–O–Cu bonds in the copper bulk with hydrogen leads to the formation of C–C molecules, C$_2$H$_x$ clusters or individual C atoms. Carbon clusters cannot be accommodated in the copper lattice. Also, in the absence of oxygen C atoms cannot easily dissolve in copper. Therefore, they have to leave the copper matrix and are expelled to the surface or to the grain boundaries. As a result, the carbonic compounds segregate to the surface and agglomerate during annealing under hydrogen. This proposed mechanism can also explain the earlier observation of the hydrogen dependency of carbon dissolution and out-diffusion in the copper film, during the growth of graphene but from the external carbon precursor. When the local concentration of carbon atoms on the copper surface reaches the supersaturation level, nucleation of a graphitic film will start.

In the case of annealing, in the absence of hydrogen, intrinsic oxygen impurities bond with carbon atoms in the bulk and form volatile CO or CO$_2$ gas to leave the bulk. This process efficiently depletes carbon and no carbon film formation occurs on the P-0 surface.

Moreover, we need to consider that the carbon and oxygen trapped inside Cu grain boundaries, voids, or any imperfection sites of Cu during the foil production or shelf life, may not even chemically bond to the Cu. Oxygen can also scavenge the carbon inside the Cu foil in the absence of hydrogen during annealing. However, introducing hydrogen into the CVD system with high enough concentration can diminish that process and keep carbon in the bulk.

The results of SEM and ToF-SIMS analyses obtained from the sample P-0-6 are also entirely consistent with the above microscopic mechanism we proposed. During the initial phase of annealing under the same conditions as sample P-0 oxygen scavenging releases the carbon from the surface. Therefore, in the second phase of annealing done under the same conditions as sample P-6, the H-assisted C depletion mechanism becomes no more relevant simply due to the absence of carbon.
Therefore, ToF-SIMS results perfectly match for P-6 and P-0-6 samples as can be seen in Figure 2. Consistent with this mechanism and ToF-SIMS results, we observe no carbon film formation detected on the P-0-6 surface in the SEM images. This test also proves that there is no role of any external carbon in the process.

### 3.2. Nucleation and Growth of Graphene from Intrinsic Carbon

The quality of the graphene film grown by CVD is directly connected with the density of nucleation sites; denser nucleation leads to smaller crystals and lower quality graphene films. Therefore, preventing uncontrolled generation of nucleation sites is essential to improve the CVD process. In this section, we explain our investigation on whether the segregation of intrinsic carbon on the copper surface may generate nucleation and growth of graphene. On the basis of our proposed mechanism, it is expected that the H-assisted C depletion during the annealing process runs at a faster rate under a higher hydrogen concentration. Therefore,

| sample     | annealing time (min) | H$_2$/Ar flow rate (sccm) | process pressure (mbar) | H$_2$ pressure (mbar) | figures | graphene surface coverage (%) | graphene nucleation density ($10^{5}$ mm$^{-2}$) |
|------------|----------------------|---------------------------|-------------------------|----------------------|---------|-------------------------------|---------------------------------|
| T-40       | 40                   | 50:500                    | 16                      | 1.4                  | 3a, S6  | 33                            | 6                               |
| T-80       | 80                   |                           |                         |                      | 3b, S7  | 63                            | 6                               |
| T-100      | 100                  |                           |                         |                      | 3c, S8, S9 | 85                            | 6                               |
| T-40E      | 40                   |                           |                         |                      | 6       | 22                            | 2                               |
| HP_T-40E   | 40                   |                           |                         |                      | 7       | 20                            | 0.2                             |

*Samples annealed under low hydrogen pressure exhibited nucleation and growth of graphene flakes instead of graphitic film formation. Sample T-40E was initially chemical etched to remove any surface carbon and then was applied the same annealing process as T-40. Nucleation and growth of graphene flakes on T-40E just as in the case of the unetched sample T-40 excludes the effect of surface carbon.*

Figure 3. SEM images of copper foil annealed under 1.4 mbar hydrogen partial pressure for prolonged annealing duration. Reduced hydrogen concentration leads to the formation of GFs. (a) T-40, 40 min annealing time. Relatively small GFs; silicon oxide particles are mostly located outside or at the edge of the GFs. (b) T-80, 80 min and (c) T-100, 100 min annealing time. The size of GFs slightly increases with the annealing time but the surface is not fully covered. Even extending the annealing time beyond 100 min leads to no significant increase. The SEM images of T-40, T-80, and T-100 in lower magnification can be seen in Figures S6–S8, respectively. (d) The Raman spectrum of six random flakes on T-100 after transferring to SiO$_2$/Si (all normalized to the G peak). The ratio of 2D/G peaks, around 2700 and 1600 cm$^{-1}$, confirm they are monolayer graphene with slight variation in their quality.
Figure 4. Effect of H-assisted C depletion mechanism on copper foil under various H_2 concentrations. Annealing in the absence of hydrogen leads to bonding of intrinsic carbon atoms with oxygen impurities, form volatile CO or CO_2 gas and leave the bulk (P-0). This process efficiently depletes carbon and no carbon film forms on the surface. Annealing under low H_2 pressure (1.4 mbar) slowly depletes the C atoms from the bulk, hence few locations on the surface could reach supersaturation and nucleation threshold leading to the formation of GFs (T-40). Annealing under higher H_2 pressure (6 mbar), the rate of C depletion is increased such that the whole surface is supersaturated simultaneously, and a disordered graphitic structure is formed without a long-range atomic order (P-6).

The formation of the disordered graphitic film on sample P-6 should be due to the rapid depletion of carbon species under relatively high hydrogen partial pressure.

Under lower H_2 partial pressure, the out-diffusion rate of C is reduced and its sudden supersaturation is inhibited. Instead, the nucleation and growth of graphene flakes (GFs) is initiated at sparsely distributed supersaturation points. In other words, this provides the growth of a graphitic layer with a longer-range atomic order. Sample T-40 was annealed under reduced hydrogen partial pressure of 1.4 mbar and for an extended annealing time of 40 min (Table 2), to attain a growth condition for GFs with a large enough size to be observed. Figures 3a and S6 display the SEM images of the surface of the sample T-40 after annealing. Rather than the disordered graphitic layer seen in sample P-6, micron-sized GFs are formed on the surface of T-40 due to the reduced carbon supply rate from the copper bulk. The rate of graphene growth is rather low, that is, after 40 min of annealing only 33% of the surface of T-40 is covered by GFs. To determine if full graphene coverage can be achieved, samples T-80 and T-100 were annealed under the same conditions as T-40 but with extended durations of 80 and 100 min, respectively. As the annealing time is increased, the GFs grew larger and surface coverages of 63 and 85% were obtained in the samples T-80 (Figures 3b and S7) and T-100, respectively (Figures 3c and S8). The Raman spectra taken from six randomly picked GFs on sample T-100 after they were transferred on to the SiO_2/Si substrate confirm the monolayer graphene structure in all flakes with slight variation in their quality (Figures 3d and S9).

To our knowledge, the formation of neither a disordered graphitic film nor graphene flakes on copper during the annealing stage in the CVD system has been reported so far. Figure 4 displays a schematic diagram that summarizes the effect of the H-assisted C depletion mechanism on copper foil under various H_2 concentrations.

No significant change in the surface coverage of GFs is observed when the annealing time was extended beyond 100 min. This can be explained as follows within the scope of the microscopic mechanism we proposed above: our results verify that carbon originating from the copper foil facilitates graphene growth, but the growth is limited by the ability of the carbon in copper to reach the surface at the annealing temperature. The diffusion rate of carbon to the surface is expected to follow a continuously declining profile as the graphene flakes grow and block the access of hydrogen to the copper bulk, suppressing the release of carbon from C–O–Cu bonds. Therefore, as the annealing time is extended, the growth rate declines and coverage tends to saturate.

Depth profiles of carbon concentration in samples T-0, T-40, T-80, and T-100, measured with ToF-SIMS, are compared in Figure 5 and its inset. As the annealing time is increased, the carbon content near the copper surface is increased while the carbon content in deeper parts is decreased. ToF-SIMS data directly and independently verifies the migration of carbon towards the surface. The inset figure shows the variation of carbon concentration versus annealing time for both near the surface (1.9–110 nm) and deeper in the bulk (110–300 nm). We observe a saturated behavior in carbon migration with respect to the annealing time, which is consistent with the saturation of graphene growth with annealing time as explained in the previous paragraph.

In the SEM images shown in Figure 3, we can see some white particles scattered on the surface of Cu samples, and their size increases with longer annealing time. These particles are a compound of silicon and oxygen, originated from the quartz tube of the furnace. It can be clearly seen that SiO_x particles are never sited at the center of GFs at the earlier stages of graphene growth. Therefore, we infer that silicon oxide particles are not the initial cause of graphene nucleation. But the accumulation and segregation of carbon atoms originating from the bulk of copper facilitate nucleation.

The model we propose in this paper based on our experimental results, provides a better understanding of why it is difficult to effectively suppress graphene nucleation without using a tuned oxygen flow in the CVD process. A diluted oxygen flow before or during the growth phase
suppresses nucleation by etching the “preformed” GFs, or carbon atoms on supersaturated spots. Hence, the number of spots which have enough agglomerated carbon for supersaturation to act as nucleation sites is reduced.

To confirm whether the origin of the observed GFs on T-40 is the carbon atoms distributed inside the bulk and not the surface contamination, we performed an experiment with the chemically cleaned Cu foils. We etched the surface of a copper foil with acetic acid/hydrogen peroxide solution to fully remove its outermost layer and the native oxide. The details of this etching process are given in the Supporting Information (Figures S10 and S11). Immediately after etching, the sample (T-40E) was annealed for 40 min in the furnace under 1.4 mbar hydrogen, similar to the process used for T-40. As demonstrated in the SEM image in Figure 6, GFs still appeared on T-40E after annealing. This provides additional evidence that carbon in the bulk of Cu foil contributes to the GF formation on the surface due to H-assisted depletion. We observed that the nucleation density of GFs was slightly reduced in the chemically etched sample as it can be seen by comparing Figures 3a and 6. We attribute this reduction to the removal of high carbon concentration in copper layers just beneath the surface by chemical etching.

3.3. Experiments with High Purity Copper Foil. Finally, we used a different type of copper foil (99.999% purity) to investigate the variation of graphene nucleation with the level of purity. We repeated annealing and chemical cleaning conditions of T-40E on a sample labeled HP_T-40E taken from the high purity copper. Even though it had 2 orders of magnitude higher purity level, nucleation and growth of GFs are also observed in this sample confirming the presence of carbon in it (Figure 7). We believe that the rolling technique should again be the cause of the carbon content. We should note that the purity level reported by the supplier refers to metallic elements. Thus, to achieve a reproducible nucleation and growth conditions, the distribution profile of carbon inside copper foil needs to be considered.

From the distribution of GFs in Figures 3, 6, and 7 we can conclude that carbon does not seem to be preferentially segregated along the copper grain boundaries. Also, in Figures 3a, 6, and 7 there are some nm size dark spots visible beside micron size GFs. We believe that these features are graphitic or amorphous carbon clusters that emerged on the surface during the cooling phase as the solubility of carbon in copper drops with decreasing temperature. On the contrary, this kind of dark spots do not appear in the SEM images of Figure 3b,c. This is due to extended exposure to hydrogen annealing, after which there was not enough carbon to emerge to the surface and form such carbon clusters during the cooling phase.
4. CONCLUSIONS

In this work, we have demonstrated the aggregation of carbon atoms on the surface of copper foil after annealing under hydrogen in the presence of external carbon sources. Depending on hydrogen partial pressure, carbon atoms may form either a disordered graphitic film or graphene on the surface. Despite the fact that the solubility of carbon atoms inside pure copper is very low, our experimental results verify that the growth of these carbon-based structures is due to the presence of intrinsic carbon in the copper bulk. We proposed that the migration of carbon atoms from inside the copper towards its surface is induced by hydrogen. This depletion mechanism is independently verified by measuring C(1d) intensity versus depth by ToF-SIMS. The depth profiles of processed and untreated samples demonstrated the migration of carbon during the annealing process under hydrogen. We conclude that the nucleation and growth of graphene on copper foil in CVD cannot be considered as a pure “surface process”, due to the presence of carbon embedded below the surface during the foil production process. Therefore, the “competition between the surface mobility of carbon ad-atoms versus desorption” of an external precursor does not define the full characteristics of the nucleation regime of graphene crystals on copper in the CVD process. One needs to include the out-diffusion of carbon atoms originated from the inside of copper bulk as well.

The carbon atoms migrating from the copper bulk to the surface can be the main cause for the nucleation of graphene crystals rather than the surface imperfections and impurities such as SiO2 particles. We believe that the prematurely nucleated and grown GFs during the annealing phase under hydrogen become a determinant factor for the density of growing GFs during the growth phase. Thus, to achieve a reproducible growth condition, the distribution profile of carbon inside the copper foil needs to be considered. Accordingly, the approach for annealing copper foil presented in this paper can be considered as a method for the initial evaluation of embedded carbon inside a copper foil and its effect for reproducing a growth recipe.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01652.

SEM images of Cu samples before and after annealing process; optical images of P-0, P-6, and P-0-6 before and after ambient oxidation; optical images of T-100 after ambient oxidation; optical images of P-0, P-6, and P-0-6 before and after annealing; SEM images of Cu samples before and after annealing.

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Notes

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