# No Graphene Etching in Purified Hydrogen

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# No Graphene Etching in Purified Hydrogen

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**ABSTRACT:** A systematic study has been conducted to investigate the role of hydrogen in the etching reaction of graphene films grown on copper foils. The results at 825 °C and 500 mTorr showed no evidence of graphene etching by purified ultrahigh purity (UHP)-grade hydrogen, whereas graphene films exposed to unpurified UHP-grade hydrogen were considerably etched due to the presence of oxygen or other oxidizing impurities. This finding reveals not only the major impact of oxidizing impurities in the graphene etching reaction, but also entails understanding and controlling the graphene chemical vapor deposition mechanism on copper substrates.



**SECTION:** Surfaces, Interfaces, Porous Materials, and Catalysis
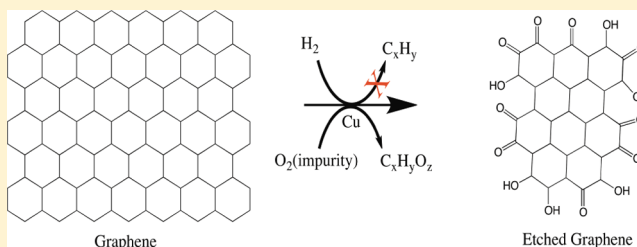
Commercial developments of graphene-based devices require a technique to produce high quality films over large areas.[1−3] To this date, graphene chemical vapor deposition (CVD) growth on copper foils exhibits great potential for mass-producing large area graphene films in a controllable and effective way.[4,5] In graphene CVD, carbon-rich gaseous species, most commonly methane, react with the metal substrate at high temperature (900−1050 °C) in the presence of hydrogen, leading to the decomposition of carbon species and the nucleation of graphene crystals.[4−6] Recently, studies demonstrated that hydrogen partial pressure and total pressure of the system are crucial parameters impacting the CVD growth of graphene.[7−11] However, the role of hydrogen, the concentration of which has been altered enormously in literature from zero[8] to thousands times the amount of hydrocarbon precursor,[7−15] has raised fundamental skepticism thus far. Indeed, studies on the role of hydrogen in graphene CVD growth concluded that hydrogen not only has a significant influence on the size and morphology of the resulting graphene domains, but can also etch graphene films.[15−17] Apart from ultrahigh vacuum CVD (UHVCVD) growth,[18−20] these experiments along with a growing number of articles in the last year suggest that molecular hydrogen is an etchant in graphene low pressure CVD (LPCVD) and atmospheric pressure CVD (APCVD), yet its presence is required for the growth.[7−12] This dual functionality as etching agent and growth activator[13−17,21] appears contradictory and improbable, since molecular hydrogen neither dissociates nor adsorbs on clean copper surfaces.[22,23] Surface science and catalysis experiments established that metals of group XI with filled *d*-levels are not versatile catalyst for hydrogenation reactions because they fail to be active in hydrogen chemisorption.[23−25] Taking these into account and examining thoroughly the results of graphene etching experiments, one

can realize a common point: the etching becomes apparent at a hydrogen pressure where the partial pressure of contaminants, (considering ultrahigh purity (UHP)-grade hydrogen) becomes comparable to the standard base pressure of LPCVD furnaces. One might then question whether the small amount of oxidizing impurities in the feedstock could be responsible for the etching reaction. We have therefore devised a set of experiments to address this important question.

In this Letter, we show using annealing experiments that hydrogen is not the culprit for graphene etching under controlled atmosphere. Instead, small amounts of oxidizing impurities are found to be responsible for graphene etching through the catalytic action of copper. In our systematic study, we have monitored graphene morphologies following annealing treatments performed under vacuum, in UHP-grade $H_2$ (99.999%, $O_2$ < 1 ppm) and in purified UHP-grade $H_2$ ($O_2$ < 1 ppb) atmosphere. Following each treatment, the graphene samples were imaged with a scanning electron microscope (SEM) and their quality assessed by Raman spectroscopy.

Graphene films were grown on 25 $\mu$m thick Cu foils (Alfa Aesar, item no. 13382) at 1000 °C in a 1.5 in. fused quartz tube at low pressure. The system consists of a manifold capable of UHV conditions where the gases are introduced into the chamber. The system's base pressure prior to gas insertion is below $5 \times 10^{-6}$ Torr. The Cu foils were heated to 1000 °C and annealed at this temperature for 30 min under the flow of $H_2$ at 50 mTorr. In order to grow graphene, $CH_4$ was introduced into the chamber, and the total pressure reached 500 mTorr. After 45 min (growth time), the chamber was cooled down to room temperature under the flow of $H_2$ and $CH_4$.[5] Graphene samples

were examined under SEM (Hitachi S-4700) prior to any treatment.

All the annealing experiments were conducted in the same CVD system at a specific temperature and pressure (825 °C and 500 mTorr), for which the highest graphene etch rate has been reported in literature.[17] In order to confirm that the vacuum level of $5 \times 10^{-6}$ Torr of our system has no effect on graphene samples at the process temperature, a control annealing experiment has been conducted. Figure 1a,b shows
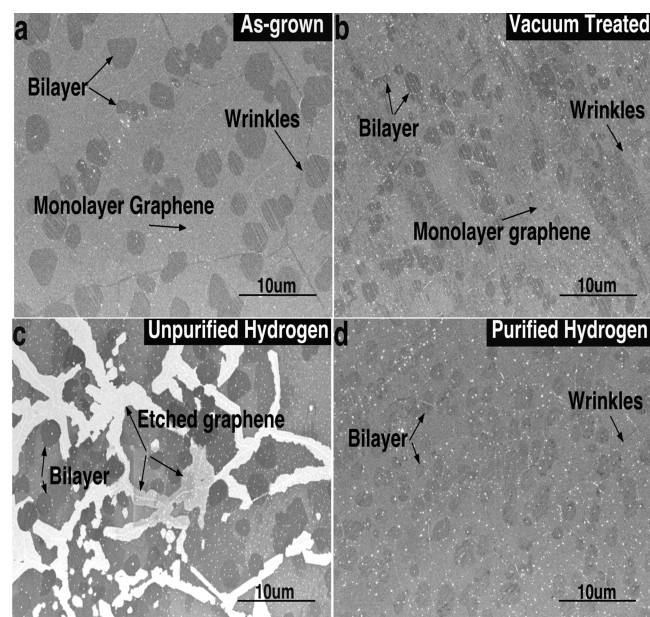


**Figure 1.** SEM images of (a) as-grown graphene film on copper foils, and annealed samples at 825 °C for 30 min (b) under vacuum, (c) in unpurified UHP-grade $H_2$, and (d) in purified UHP-grade $H_2$.

the SEM images of the as-grown graphene film on copper and the vacuum annealed samples, respectively, demonstrating continuous, uniform, and large area graphene films in both cases. Samples were then exposed to a flow of as-received UHP hydrogen at 825 °C for 30 min maintaining a system pressure

of 500 mTorr during the process. SEM images from the samples exposed to the flow of unpurified UHP grade hydrogen show etched areas similar to what has been previously reported by Zhang et al.[17] (Figure 1c). In order to observe the true effect of hydrogen and test our hypothesis on the role of oxidizing impurities, a hydrogen purifier (DEOXO, $O_2 < 1$ ppb) was installed to provide purified hydrogen from the same hydrogen bottle used in the previous process. The same $H_2$ treatment described above was then conducted with purified UHP grade hydrogen on as-grown graphene films. Samples examined under the SEM showed no evidence of graphene etching from purified UHP-grade hydrogen (Figure 1d).

To further examine the results and confirm our hypothesis, as-grown, vacuum, unpurified, and purified UHP-grade hydrogen treated samples were transferred onto a 100 nm $SiO_2/Si$ substrate using the transfer technique reported in ref 26. Figure 2a−c shows SEM images from the transferred as-grown, vacuum, and unpurified UHP-grade hydrogen treated samples, respectively. As shown previously in Figure 1c, it is evident that the graphene film annealed in unpurified UHP hydrogen has been etched from some areas, mostly along the wrinkles. The etching exhibits anisotropic behavior similar to what has been previously reported by Zhang et al.[17] Note that no correlation between the presence of bilayer domains and etching is observed. Figure 2d is an SEM image from a graphene film annealed in purified UHP grade hydrogen and then transferred on a $SiO_2/Si$ substrate. The graphene layer is uniform and continuous over a large area, and has not been substantially modified by the annealing treatment.

Raman microspectrometry measurements (Renishaw Invia, $\lambda$ = 514 nm) have been carried out on the transferred graphene to determine the number of layers as well as the quality of graphene films. Figure 2e presents typical Raman spectra averaged from 400 points collected over the surface of each sample. The intensity ratio of peak 2D over G ($I_{2D}/I_G$) is ~3.2 and the 2D peak has a full width at half-maximum (fwhm) of ~27.5 cm$^{-1}$, confirming the formation of single-layer graphene (SLG).[5,14,26] The D peak, associated with the presence of defects in the graphene, has a very low intensity, indicating that the graphene film maintains high quality after transfer.[26] The Raman spectrum from the purified UHP-grade hydrogen
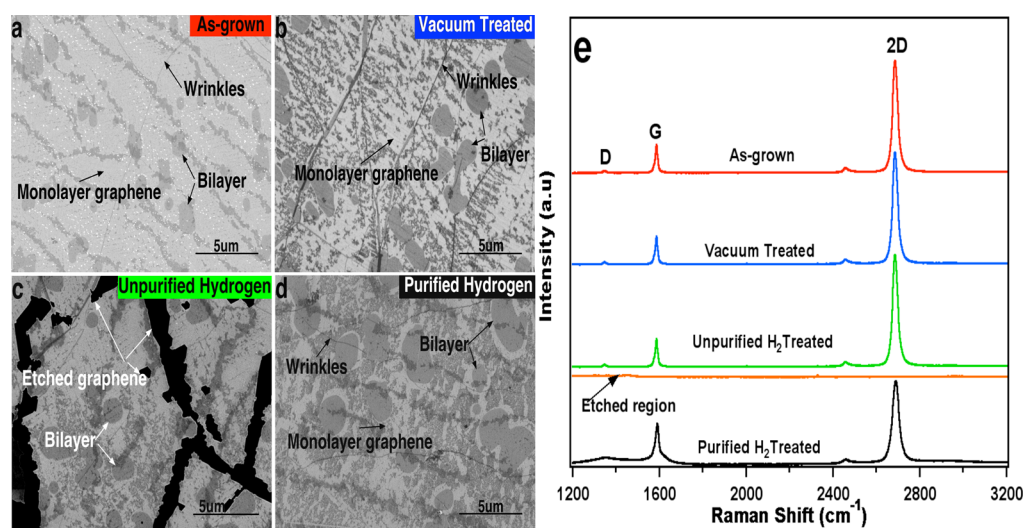


**Figure 2.** SEM images from CVD graphene transferred on $SiO_2/Si$ substrate: (a) as-grown, (b) vacuum, (c) unpurified, and (d) purified UHP-grade $H_2$ treated samples. (e) Raman spectra ($\lambda$ = 514 nm) from as-grown, vacuum treated, unpurified, and purified UHP-grade $H_2$ treated samples.

treated graphene film exhibits a broadened D peak at ~1350 cm$^{-1}$, which is indicative of the presence of amorphous carbon.[27] However, no significant change has been observed in the case of films treated in unpurified UHP grade hydrogen. The comparison of these spectra highlights the role of oxidizing impurities in the feedstock for etching amorphous carbon. Considering that previous studies have formally established the existence of preferential etching at growth-induced defects,[28,29] it appears clear now that it is important to control the oxidative impurities for optimizing the growth conditions required to produce high quality graphene.

To highlight the role of copper, we have also conducted identical annealing studies with unpurified hydrogen for graphene films transferred on SiO$_2$/Si substrate. No etching was observed, which is in agreement with studies reported in the literature.[14,17] This phenomenon suggests that oxidizing impurities do not etch graphene films directly at this temperature (825 °C) and that the substrate plays an active role in the etching process. The oxidation mechanism of graphene on metals has been elucidated for Ru and Ir supports.[29−31] The preferential etching of graphene on those metals starts at point defects and edges, and is visibly enhanced due to their catalytic activity for the oxygen dissociation.[29−31] On copper, the etching mechanism appears similar, although further investigation will be required to identify the etching pathways.

Our findings show that the existence of various graphene CVD growth recipes can be explained by considering differences in conditions from furnace to furnace. Various sealing conditions, different level of contaminants in gas lines, and most importantly, process gas purity are key parameters in defining the optimum growth conditions. The effect of these growth parameters is evident in the original graphene CVD growth recipes,[5] where a continuous flow of methane and hydrogen is kept during cooling down in order to yield uniform and continuous graphene films.[5,6,16,17] Considering the role of oxidizing impurities identified here, the CH$_4$/H$_2$ flow appears necessary for preventing etching, most likely by the means of a competitive action with carbon growth. This surprising chemistry was investigated further by performing additional experiments in which the methane flow was turned off during cooling down, leaving only purified UHP-grade hydrogen in the CVD system. As expected, the SEM images showed continuous, uniform, and large-area graphene. Moreover, we have performed similar CVD growth studies with solely methane, serving a double role: copper oxide reducer and carbon supply for growth. The results showed noncontinuous and etched films of graphene. This can be explained considering graphene etching by oxidizing impurities in a UHP-grade methane bottle (O$_2$< 15 ppm). These results, to be reported in details elsewhere, further confirm the significant impact of the presence of oxidizing impurities in the feedstock for the growth of graphene on copper substrates.

In summary, our results show no evidence of graphene etching in purified hydrogen. On the contrary, they prove that oxidizing impurities are responsible for etching reactions. We also report that the catalytic role of copper is not only essential in the growth process but also during etching. The amount of oxidizing impurities can no longer be ignored in future growth recipes since they control the balance between growth and etching, which is crucial for further improving graphene film quality and developing large single-crystal graphene layers.

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**Notes**
The authors declare no competing financial interest.

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