# Parameter Sensitivity of the Chemical Vapor Deposition of Graphene on Cu

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Amontree et al. recently reported on the chemical vapor deposition (CVD) synthesis of graphene on $Cu$ and the influence of contaminating oxygen [1]. The parameter dependency on the CVD kinetics was investigated at 900 – 1000°C in the low-pressure regime, where the kinetics revealed graphene formation from a pre-equilibrated $CH_3(ad)$ phase. Contaminating the gas feed with oxygen in the sub-ppm regime was shown to affect the outcome of the CVD synthesis. However, the authors missed discussing their findings regarding the current knowledge of graphene CVD growth on $Cu$ and overlooked that their data follows a general trend in growth kinetics, which is reviewed in our commentary. We also suggest that the interplay of oxygen with $Si$ contamination accounts for the observed influence of sub-ppm oxygen contamination on graphene growth kinetics. Such $Si$ contaminations have been reported to originate from the quartz reactor walls during conditioning and lead to the segregation of $SiO_x$ in the presence of oxygen.

Amontree et al. state that "…there is not a well-accepted quantitative model of the growth kinetics that can be used to guide synthesis" which is only partly true. Many of the early kinetic models lead to qualitative or semi-quantitative descriptions [2-4]. However, the kinetic model of Kim et al. connected kinetics with thermodynamics, assuming growth from a pre-equilibrated carbon feeding phase, which allowed for a quantitative description [5]. At that time, the experimental control of the nucleation density and the graphene flake shape was not available, and the model contained a phenomenological term to account for the irregular flake shape and island distribution at high coverage.

In 2012, ways of reducing the nucleation density were reported [6-9]. We could show in a later study why oxygen pre-treatments of Cu foils reduce the flake density at the beginning of the synthesis to values below 1 flake per mm2 support area [10]. A pressure regime was identified where graphene flakes grow as isolated, regularly shaped hexagonal islands. The surrounding, graphene-free $Cu$ foil hosts a pre-equilibrated 2-dimensional feeding phase of adsorbed $CH_x$ proceeding along the following reaction:[11]

$$CH_4(g) \rightleftharpoons CH_x(ad) + \left(2 - \frac{1}{2}x\right)H_2(g) \qquad (1)$$
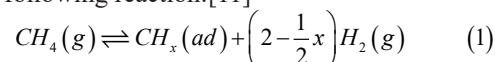
Equation (1) describes the equilibrium concentration of the $CH_x$ adsorbate on the catalytic $Cu$ surface, from which a small number of adsorbates are removed at a low rate to feed the growth of graphene flakes. Comparison of the experimentally observed flake increase per time (graphene growth speed) with the scaling of the applied methane and hydrogen partial pressure during the CVD process allows to extract the value $x$. Thus, experimental data can be used to identify which $CH_x$ adsorbate is the pre-equilibrated carbon feeding phase of the growing graphene island. Obviously, graphene growth sets in only if growth is thermodynamically favored. In a subsequent study, we precisely mapped the thermodynamic stability regime of the CVD growth of graphene on $Cu$ by monitoring the flake shape to a growing (hexagonal) island or a decaying (round) island, which, in addition, showed etching pits inside the island when being thermodynamically unstable [12].

With the extracted thermodynamic potentials of the graphene formation reaction, the stability region for the formation of graphene on $Cu$ and the deviation from thermal equilibrium during graphene synthesis can be quantified and visualized in a CVD parameter diagram. Using this information, a kinetic model was formulated that precisely predicts the flake growth velocity with a precision better than 20% when applying CVD reaction in the total pressure regime of 10-500 mbar while not deviating more than 2 orders of magnitude from the thermodynamic equilibrium [13]. If these prerequisites are met, the pre-equilibrated feeding phase was shown to be a 2-dimensional gas of adsorbed carbon atoms ($x = 0$ in equation (1)) as confirmed by comparison with literature data. The isolated graphene flakes maintain their hexagonal shape during growth, allowing for a microscopic description based on $C(ad)$ impingement at and detachment from each
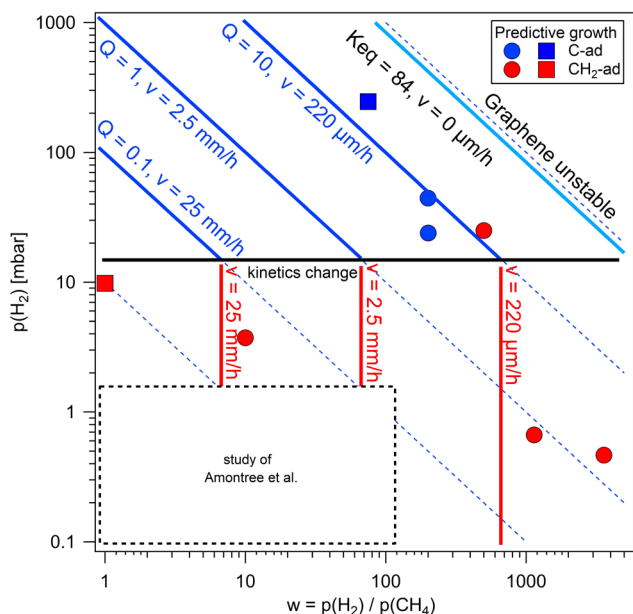
***Figure 1.*** *CVD parameter chart visualizing the graphene growth kinetics on Cu at 1020°C. At elevated pressure, growth proceeds from pre-equilibrated C(ad) (blue lines) while, below ~ 10 mbar, the pre-equilibrated feeding phase changes towards $CH_2(ad)$ (red lines), overcoming a reduced activation energy barrier. The trend continues below ~ 1 mbar CVD pressure as shown in the study of Amontree et al. where a $CH_3(ad)$ phase feeds graphene growth at an even further reduced apparent activation barrier. The figure is adapted with permission from ref.[15]. Copyright 2023 American Chemical Society.*

atom of the flake perimeter. Note that this growth model does not contain meaningless fit parameters but provides reasonable attachment/detachment rates of a growing graphene flake. In addition, the determined reaction entropy could be used to calculate the extremely low coverage of the feeding $C(ad)$ phase on *Cu* during CVD synthesis. This explains why the reaction is sensitive to carbon contaminants [14].

Amontree et al. provide a formal kinetic model in their supporting information without mentioning that it is identical to the formula derived by Kim et al.[5] and the more general description of us [11,13,15]. Comparison with experimental data collected similarly as in the kinetic study of refs [11,13] proves a pressure scaling of the graphene formation kinetics indicating growth from a pre-equilibrated $CH_3$(ad) feeding phase ($x = 3$ in eq. (1)). In ref. [15], we reported that the kinetics of the graphene synthesis reaction change when conducting the CVD growth at ~ 1000 °C and pressures below 10 mbar. The pre-equilibrated feeding phase changes from $C(ad)$ towards $CH_2(ad)$ accompanied by a substantial reduction of the apparent reaction barrier from $(5.65 \pm 0.3)$ eV for $C(ad)$ attachment to the g-island to the equivalent barrier of $(3.2 \pm 0.4)$ eV for pre-equilibrated $CH_2(ad)$. Figure 1 displays a chart for CVD synthesis at 1020°C similar to the ones shown in ref. [15]. Blue lines indicate the flake growth velocity during CVD synthesis from a pre-equilibrated $C(ad)$ phase, and red lines for the predicted growth from pre-equilibrated $CH_2(ad)$ at reduced barrier height. Red and blue squares (ambient pressure CVD) and circles (low-pressure CVD) indicate literature data that fit the predictions of the kinetic model. The dashed box sketches the CVD parameter range investigated by Amontree et al., where the experimental data do not match the description of a pre-equilibrated $CH_2(ad)$

phase feeding the graphene growth, but a pre-equilibrated $CH_3(ad)$ phase at an apparent lower barrier of 2.8 eV or 1.7 eV in the presence or absence of hydrogen, respectively. The authors fail to discuss that the barrier of 1.7 eV matches the experimentally determined value of the $CH_4$ decomposition reaction toward $CH_3(ad)$ on *Cu*, which would prove a non-activated incorporation of $CH_3(ad)$ to the growing island [16]. In ref. [15], we provide the extrapolation of the energy barriers of the methane decomposition reaction at typical CVD synthesis temperatures, finding that the attachment processes are rare when compared to the number of events taking place during CVD synthesis at higher total pressure. Note that the rate of rare attachment events with a lower energy barrier is readily overtaken by competing impingement processes at increased attempt frequency, even if they have to overcome a higher attachment barrier. Following the argumentation along this line, the data of Amontree et al. support this microscopic picture, indicating that rare attachment events (of $CH_3(ad)$) at the growing graphene islands start to play a role when restricting the carbon content of the gas feed.

Amontree et al. report that in the presence of oxygen, initially, graphene flakes grow but vanish at a later stage so that at long enough synthesis times, no graphene is grown on the *Cu* surface at all. Here, the authors neglect that a reaction consisting of a growing and etching term cannot deliver such a behavior: either the g-growth rate exceeds the etching term, leading to the formation of graphene, or no graphene is synthesized at all. Thus, the observation that at first, graphene is synthesized, followed by its decomposition at a later stage, indicates that the catalytic reactivity of the system changes during growth.

In a very recent study, [17] we identified the most likely reason for this behavior. Amontree et al. mention that the reactor was exposed to a hydrogen flow at 1090°C to clean the quartz tube after bakeout. We found that such high temperatures at elevated hydrogen pressure lead to the deterioration of the quartz reactor. The reactor wall then readily releases *SiO* during synthesis at temperatures above 1020°C which is transported to the *Cu* foil where it is reduced and dissolved in the Cu foil bulk. However, if oxygen is available at elevated temperatures, adsorbed oxygen drags the dissolved *Si* to the *Cu* foil surface, forming silica. As long as *Si* is available, the adsorbing oxygen is immobilized at the silica surface and does not attack the growing graphene, making it seemingly resistant to oxidation. However, when the bulk dissolved *Si* is exhausted, adsorbing oxygen will attack the growing graphene and remove it from the catalytic substrate, changing its catalytic properties by the covering surface silica phase. With the help of these findings, the initial growth followed by the removal of the CVD-grown graphene can be understood. It also identifies the surface phase observed by scanning tunneling microscopy as a surface silicon oxide, [1] which was identified in recent XPEEM studies [17,18]

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