Time evolution of the growth of single graphene crystals and high resolution isotope labeling

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A B S T R A C T
We developed a method of precise isotope labeling to visualize the continuous growth of graphene by chemical vapour deposition (CVD). This method allows us to observe, as a function of time, the growth of graphene monocrystals at a resolution of a few seconds. This technique is used to extract the anisotropic growth rates, as well as investigate the formation of dendrites, and the dependence of growth rate on adsorption area of methane on copper. This technique also gives precise start times for individual graphene nucleation sites. We obtain a physical picture of the growth dynamics of graphene and its dependence on various parameters. Finally, our method is relevant to other CVD grown materials. © 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene is a two dimensional material which has attracted a great deal of attention for its unique physical and electronic properties [1–3]. Originally isolated by mechanical exfoliation of graphite [4], more scalable methods necessary for production of large scale graphene layers and industrial applications include chemical vapour deposition [5,6] and graphitization of SiC [7]. Chemical vapour deposition (CVD) of graphene sheets on commercial polycrystalline copper foils is a leading candidate for the production of large high quality graphene films. One of the challenges in producing high quality graphene by CVD is controlling the nucleation density of graphene crystals which in turn limits the size of individual crystals. Grain boundaries where different misoriented graphene crystals come together are known to reduce the mechanical strength and electronic properties of graphene [8,9].

Since the pioneering work of Li et al. in graphene CVD on copper foils [6] a great deal of work has been done in determining the optimal conditions to produce large single crystal graphene and understanding the role of various growth parameters in the CVD process [10]. This has led to large gains in the size and quality of single crystal graphene flakes which can be produced [11,12] up to mm and cm scales. Analyzing and understanding the growth dynamics of CVD graphene, is one of the main contributions of this work.

Previous works studying graphene CVD growth dynamics have been done. These have either relied on in-situ LEEM measurements [13–16] or been done using an alternating isotope labelling method employing fewer than ten time intervals [10,17,18]. In our work we developed a method to continuously image and recreate the crystal growth ex-situ, i.e., after the crystal is fully grown. This is achieved by varying the relative ratio of the isotopes continuously during the growth process. The isotope concentration will therefore provide a unique label determining when the material was grown. This method is similar to carbon dating, where the isotope concentration of radio active carbon decays over time and therefore allows the dating of organic materials [19]. The difference here, are the time scales involved (seconds) versus hundreds of years and the spatial dependence, which allows us to correlate the position with time.

Our method of continuous isotope labelling is less technically demanding than in-situ LEEM measurements, and compared to previous isotope labelling methods represents an order of magnitude improvement in the number of discernible time steps (less than 10 vs. greater than 80). This allows us to probe the dynamics of CVD growth on copper in more detail than was previously possible. This technique is used to extract new information on dendrite formation and quantify the effect of adsorption area of methane on copper, as well as extract data on the nucleation time of specific crystals and build up movies of the CVD growth process.

The ability to visualize the growth of atomic materials has important implications, particularly with the recent development
and potential of hybrid materials beyond graphene [4,20], where the atomic layering and growth history is an important factor. For graphene, in particular, this method not only gives new insights on the growth dynamics, like the formation of dendrites, of nucleation sites or additional layers as discussed here, but the varying isotope method can also be used to label certain areas of the crystal without changing its electronic properties. Other applications include the possibility to tune the nuclear spin density [21], the ability to do phonon engineering [22], reduce thermal conductivity due to phonon disorder [23], determine chemical and vibrational properties of different layers [18], increase sensitivity to determine specific phonon modes [24], and others [25–27].

Here we provide new results organized along three main themes: continuous labeling and determination of the sensitivity of the method, which can provide close to hundred independent labeling or time steps; dynamic growth or the making of movies and time snapshots of the growth, in particular the fractal growth of graphene; growth rates and the dependence of the growth rates on anisotropy, dendricity and growth diffusion area.

2. High resolution continuous labeling method

In general, the possibility to label a material locally is of importance in a number of applications. Indeed, it allows information to be encoded, without modifying the basic properties. In the case of graphene, this can be particularly useful in areas where transparency, organic composition or low mass is important, such in labeling electronic devices or biomolecules. The labeling is done by using different relative concentrations of isotopes, which can then be used for encoding or transparent labeling. The detection is achieved by Raman spectroscopy, which is used to characterize graphene [28] and other graphitic materials [29]. Here we use a combination of precisely controlled isotopic methane flow [12C and 13C] and Raman mapping to probe the growth dynamics of graphene crystals in much greater detail than is possible when using only a binary on/off isotopic variation method [17].

Several samples were prepared using pure 12CH4, pure 13CH4 and various mixes. The exact growth conditions are detailed in the supporting information. In the 13C carbon isotope graphene we observe a downshift in Raman peak position by a factor of approximately 0.5, which is not achievable with the 12C concentration increasing with time. The analysis could not be done to a linear function with

\[ \Delta \omega = \omega_{2D}^{12C} - \omega_{2D}^{13C} \]

where \( \omega_{2D}^{12C} \) and \( \omega_{2D}^{13C} \) are free parameters and gives values of 2686.7 cm\(^{-1}\) and 2580.6 cm\(^{-1}\) respectively.

The theoretical line plotted in Fig. 1c shows the expected result taking \( \omega_{2D}^{12C} = 2687 \) cm\(^{-1}\). The excellent agreement quantifies the precision with which the isotopic ratio of our graphene during CVD growth and extract this value by Raman spectroscopy of our samples. The average standard deviation for the peak position for a given concentration is \( \sigma = 1.4 \) cm\(^{-1}\). This translates into a labeling resolution of

\[ R_l = \sigma / \Delta \omega \approx 1.3 \times 10^{-2} \]  

(2)

The high resolution allows the labeling of 1/Rl = 80 regions independently. Moreover, most physical properties are not affected by the labeling, except for Raman process. This can be used for a very small amount of samples, such as encryption, variable nuclear spin concentration, or even isotope concentration detection. In what follows, we will use it in order to gain insight into the growth mechanism of graphene.

3. Dynamic imaging

CVD growth using isotopic methane is a useful tool to characterize the growth of polycrystalline sheets [6,17] and graphene single crystals. Typically this has been done by using alternating flow of 12C and 13C methane to produce graphene which displays a tree-ring like growth pattern [6]. Here, several grapholcon samples were prepared with the ratio of 12C to 13C varying linearly as a function of time. Sample B, shown in Fig. 3, was first annealed in hydrogen at 1073 K for 4 h to prepare the surface and then graphene was deposited during a 400 s growth phase with a combined methane flow of 1.2 sccm. The flowrate of 12CH4 and 13CH4, as well as the isotopic ratio are shown in Fig. 2 as a function of time. Since the Raman peak position is proportional to the isotopic concentration (Fig. 1), we can then extract the expected 2D peak position at any given time using eq. (1).

The growth conditions employed for this sample were designed to give an incomplete growth with dendritic grapholcon [30]. A Raman map was taken with grid spacing of 900 nm. A spectrum was taken at each point on the grid with a collection time of 1 s. The position, width and intensity of the 2D peak were then extracted. We observe that the 2D position is lowest at the center of the grapholcon and increases as we move towards the edges. This is consistent with a growth that begins with primarily 13C methane, with the 12C concentration increasing with time. The analysis could equally be performed using the G or other Raman graphene peak, however the 2D peak was chosen for the combination of large amplitude and high Raman shift, which enable the position of the peak to be extracted with greater precision and lower collection time relative to other peaks. We also observe in the center of the graphene crystal a region of bilayer graphene, characterized by a double Raman peak structure. The growth times for each graphene layer are calculated from the position of the two independent 2D peaks observed. In fact, we observed two types of bilayer growth, either Bernal stacked or not, sometimes even in the same crystal. In the case of Bernal stacking, the 2D Raman peaks of each layer hybridize [31] to form one peak corresponding to the average mass between the two layers, while in the non-Bernal stacking, the two Raman peaks identify the frequencies corresponding to the respective atomic mass of each layer, with a weak enhancement due to graphene enhanced Raman scattering [32]. This is indicated in Fig. 3 where the bilayer is shown in orange. In the last square of Fig. 3 we show only the contribution of the first Raman peak corresponding to the first layer.

This linear shift in peak position allows us to extract an absolute time scale for the progression of the crystal formation. We can visualize the growth of the grapholcon as a function of time by considering the points in the Raman map with \( \omega_{2D} < \omega_{2D}^{12C} \). In Fig. 3 we show snapshots of the grapholcon at 8 different points in time. In the supplementary material the full movie of the graphene growth is shown.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.09.034.
3.1. Bilayer growth

We observe two different behaviours in the formation of bilayer graphene, which are reflected in their Raman spectra. Either with the two layers acting as independent single layers where we observe a double peak structure in the 2D band or as a bernal bilayer where we observe a single peak whose position corresponds to the average carbon mass of the two layers.

The behaviour is correlated with the apparent relative orientation of the two layers. If the two crystals have the same orientation we observe Bernal stacking evidenced by the decrease in intensity of the 2D peak combined with a large increase in peak width. This is consistent with the behaviour of bernal stacked exfoliated graphene, where we observe decreased intensity and increasing width in the 2D peak [31].

We also observe bilayers where the two layers are offset by approximately 30°. In this case the layers behave as independent bilayers and we observe a double peak structure with a large intensity of the 2D peak relative to the G peak. Both of these findings are consistent with previously reported orientation dependence of the 2D peak [33].

Some bilayers display both types of stacking in regions, as seen in Fig. 4. In this case we see an obvious difference in the 2D/G ratio for each of three distinct regions, as well as the breaking of the 6-fold symmetry of the 2nd layer in the region that is not bernal stacked. We shows also a representative spectra from each region and note that they are distinct in the total number of peaks, peak width and intensity, allowing us to easily determine the type of stacking by Raman spectroscopy.

Using these spectral signatures to determine the stacking order we took a sample of 50+ bilayers across three different samples found that Bernal stacking is preferred by a ratio of approximately 2:1. We also note that for both bilayer types we observed decreased growth rates and delayed nucleation times relative to the first layer of graphene.

4. Growth rates: anisotropy, dendricity, and diffusion area

It’s clear from the isotope labelling that the graphene crystal grows from the center outwards. This is consistent with previous studies on CVD graphene growth [17,34,35]. In some of these studies the crystal symmetry was also determined and various shapes have been observed, including four-fold and six-fold symmetries, depending on the growth conditions and substrate [36]. However, the local growth rates have not yet been analyzed. Using our data from the method described in section 3 we are able to extract the growth rates and directions at every point in the crystal.

4.1. Anisotropy

The growth anisotropy is not affected by the growth stage and is
constant over time during the growth and independent of the size of the crystal. The radial growth is indeed linear with radius (see Fig. 3a) and therefore time, since we chose $x \sim t$. The $^{12}$C and $^{13}$C methane flows are calibrated, so that the total methane flow is constant over time to allow for a precise determination of the time dependence. To analyze the anisotropy in more detail, we compare the growth rate in different directions for a weakly dendritic graphene crystal, shown in Fig. 5b. This sample was prepared with a combined CH$_4$ flow rate of 1.2 sccm and a H$_2$ flow rate of 80 sccm, during a 3 min growth phase. The highest growth rates are clustered along 6 arms spaced by roughly 60°. By taking profiles along the fastest and slowest directions we observe that the average growth rate is linear with radius.

**Fig. 3.** Sample B. Visualizing the growth of a graphene crystal: Snapshots of the graphene growth showing the combined intensity of the 2D peak as a function of time. Intensities are scaled to differentiate between layers 1 and 2. Last square: Raman maps of a dendritic graphene crystal indicating the Raman shift of the 2D peak and associated time from the peak position to time correspondence. Only the layer 1 peak position is shown. (A colour version of this figure can be viewed online.)

**Fig. 4.** Sample B a) High resolution Raman map showing the relative intensity of the 2D and G peaks of a bilayer region in the center of a graphene crystal. The markers correspond to the location of the spectra shown in b) spectra representing the three distinct regions or monolayer, Bernal bilayer and independent bilayer. We note a double peak structure in the G band for both bilayers as well as different behaviours of the 2D peak depending on stacking type. (A colour version of this figure can be viewed online.)
growth rate is roughly doubled along the fast profiles when compared to the slow ones, 9.0 μm/min vs 4.7 μm/min.

The growth rate was extracted for growths performed across a range of methane gas flows. Comparing the calculated partial pressure of methane gas with the growth rate we observe a clear linear relationship. Fig. 5c shows the relationship. In all cases this data was measured along the fastest growth direction, and includes samples prepared using the $^{13}$C/$^{12}$C technique discussed in this article as well as pure $^{13}$C samples where the growth rate is calculated from the diameter of the graphlocon and the growth time. To probe whether this relationship holds within the same single crystal, we synthesized sample F using a variable overall methane flow as well as shifting the $^{13}$C/$^{12}$C ratio and the same range of growth rates as those extracted from individual growths was obtained.

4.2. Fractal shape and dendircity

In Ref. [30] it was shown that fractal graphene crystals can be synthesized using CVD. Fractal shapes can lead to an enhanced broadband efficiency in antenna designs [37] and the corresponding increased edge to surface ratio, can lead to an enhanced reactivity for chemical processes at the edge [38]. Pushing the anisotropy further could even lead to the synthesis of quasi one dimensional arms or graphene nano-ribbons.

A large dendritic sample was synthesized using low pressure and low gas flow rates. The copper foil was sonicated in acetic acid for 30 min prior to growth in order to suppress graphene nucleation and allow larger domains to form. A high resolution Raman map shows details of the formation of the dendirctic arms of the graphlocon crystal. The growth rates were extracted along the primary arm of the crystal as well as several dendrites and shows the dendrites forming concurrently with the main arm. The average linear growth velocity is extracted by fitting the distance along each profile to the time corresponding to the 2D peak position at each point on the profile. We see that the main arm has a velocity of 18 μm/min while the dendrites on the side arms have a slower average velocity 11–12 μm/min even though this is along the “fast” direction. If we slice our data more finely we can see that many of the dendrites in fact show an accelerating growth rate. This increasing growth rate as the dendrites become more pronounced suggests that the growth is dependent on the local available copper surface, which we discuss in more detail in the next section. A similar analysis was performed for several different samples. All samples were produced using a similar low pressure CVD growth, but with small variations on the conditions. From the Raman maps of these samples we can extract the area and perimeter of the graphlocon as a function of time.

We consider the scaling exponent $\alpha$ defined by $A \propto P^\alpha$, where $A$ is the area and $P$ the perimeter. A compact hexagon would give $\alpha = 2$, whereas for a more dendirctic shape the value should be lower [39]. In previous works, various scaling exponents have been extracted, ranging between 1.43 and 2 for different flakes under different growth conditions and particularly sensitive to growth temperature [30]. In these works, $\alpha$ could only be extracted once at the end of the growth for every grown crystal. Here, on the other hand, we are able to determine how $\alpha$ evolves during the growth process. We see that the scaling exponent doesn’t change as a function of time as shown below. This means that the growth conditions determines $\alpha$, which is time-invariant, while the growth time simply determines the final size of the crystal. Hence, for a dendirctic crystal, the growth rate in the fastest direction is not constant, but $\alpha$ is.

In Fig. 6b we show the area versus perimeter of 4 different graphene crystals. A powerlaw fit gives values of $\alpha$ ranging from 1.4 to 1.98 for the scaling exponent. The range of validity of a single powerlaw extends over the entire size of the crystal, demonstrating the time invariance of $\alpha$ during the growth process. We also note that the fractal dimension increases with an increasing ratio of hydrogen to methane during the growth. In one case (sample C) we obtain a value of $\alpha$ considerably larger than for the other samples. This sample, also shown in Fig. 5b, was prepared with a much larger hydrogen flow of 80 sccm when compared to all the other samples, which ranged from 4 to 12 sccm $H_2$ and leads to fewer dendrites and $\alpha \approx 2$.

4.3. Diffusion growth area

Earlier studies have already examined the time dependence of dendrite growth and merging in graphene and found that growth is faster at the tip of the dendrite and slower for regions in between dendrites and slower at the end of the growth [34].

We observe a similar effect. Fig. 7a shows the Raman map of a fully covered graphene sheet grown using a linear isotope shift, sample G. The growth rate is taken along many different profiles and we see that as we approach a grain boundary the growth rate slows considerably. In this sample the typical growth rate is in the range of 20–30 μm/min whereas near the boundaries it drops below 10 μm/min.

To gain insight into this process we analyze sample D, the dendirctic graphene crystal shown Fig. 6a. We show that the growth rate correlates with the locally available copper surface and argue that the dendirctic growth is limited by the diffusion of the adsorbed C species on the available copper surface. We estimate the related diffusion radius to be 6 μm as discussed below.

We extracted the growth rate along many different profiles along the edge by focusing on the fastest growth direction. From
the high resolution raman map we can obtain for any given time \( t \), the exact shape of the graphlocon as well as the growth rate in any direction. In Fig. 8 we see two examples illustrating results for different dendrites. The top line shows the behaviour of a dendrite growing into free space. As the dendrite grows the shape becomes more pronounced and the available copper surface increases. This results in an increasing growth rate. The second line shows a dendrite growing into occupied space. In this case as the dendrite grows the available copper surface is decreasing and the growth rate is limited by the lack of available surface. This results in a decreasing growth rate. The correlation between the locally available copper surface and the growth rate was averaged across 20 dendrites. We observe an approximately linear relationship above 30% available surface and a roughly constant growth rate of 5 \( \mu m/\text{min} \) below 30%.

In order to determine the approximate radius of the diffusion area we first assume that the growth rate is a linear function of free surface area over the range of 30%–70%. We fit the data in that range considering radii from 1 to 20 \( \mu m \) and extract the coefficient of determination \( r^2 \) for the linear regression. The radius corresponding to the maximum \( r^2 \) determines our diffusion radius, which we find to be approximately 6 \( \mu m \). This value is similar to the observed spacing of dendrites seen in Fig. 6a. The mechanism emerging from this, is that the methane is adsorbed on the copper surface and then diffuses on that surface. Once a graphene nucleation has started, the edge of the crystal requires more methane while at the same time expelling the accumulated hydrogen from the copper induced catalytic conversion of methane to carbon. The rate of this reaction depends on the local concentration of hydrogen and methane gases. The more methane is available within its diffusion area, the faster the growth of graphene.

### 4.4. Nucleation dynamics

Control of graphene nucleation is critical in the production of high quality monocrystal graphene. Suppressing nucleation is a critical component in synthesizing large scale graphene crystals [40]. Previous studies on the effects of different parameters on nucleation density have shown it to depend on a number of factors including copper surface morphology [41], preprocessing [42,43] and growth parameters [10,44]. However all of these studies are limited by a lack of fine grained time information and an absolute time scale and cannot establish exactly when nucleation occurs.

Here we show that graphene nucleation is time dependent with individual crystals nucleating at different times independent of other factors. The absolute time scale provided by our labeling allows us to extract the exact nucleation time of individual graphene crystals and to understand the size dependence of graphene crystals in a given sample as a function of their nucleation time. Our results also show that smaller single layer graphene crystals form as a result of delayed nucleation and that the mechanism and growth rate are the same for both smaller and larger crystals. Indeed, Fig. 9a shows two crystals growing in the same area. The colormap clearly indicates that the large crystal nucleated earliest and the smaller nucleated at a later time.

By extracting the growth rate along several profiles we can see that the rate is consistent across the larger and smaller crystal but that the nucleation time, indicated by the peak position at the

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**Fig. 6.** Sample D a) Extracting the average growth rate of the primary arm and several dendrites of a large graphlocon b) Perimeter and area of the graphlocon as a function of time for several samples prepared with different growth conditions. Data points are offset on the y-axis to show the difference in slope, such that the area of samples C, B and E are scaled by factors of 8,4 and 2 respectively. (A colour version of this figure can be viewed online.)

**Fig. 7.** Sample G a) Raman map showing the 2D peak position of a full coverage graphene growth b) growth rates extracted from the map show a sharp decrease as crystals merge together. (A colour version of this figure can be viewed online.)
center of the crystal is much later in the small crystal. We can conclude that the large graphlocon formed starting immediately upon introduction of methane into the three minute CVD process whereas the smaller crystals did not begin until approximately 1 min later. In contrast, the growth rates extracted from both crystals are very similar and approximate $8-9 \mu \text{m/min}$. The origin for the different nucleation times could be the result of impurities, which are deep inside the copper and that slowly diffuse to the

![Figure 8](image1.png)

**Fig. 8.** Sample D. Top: Example of an accelerating dendrite. Filled green circle indicates the free copper surface, $S_0$, while the arrow indicates the magnitude of the growth velocity, $v$. Middle: Growth velocity as a function of time, with large circles indicating the snapshots shown. Bottom: an example of a decelerating dendrite. A full movie can be seen in the supplementary material. (A colour version of this figure can be viewed online.)

![Figure 9](image2.png)

**Fig. 9.** Sample B. a) Different size crystals are shown to start at different times, by taking line profiles on crystals of different size we show that the growth of the larger crystal started earlier than the smaller crystal. b) Linear fit to the profiles shown in c shows that the data is well fitted to a constant growth rate and gives both the growth rate and start time of the two crystals. (A colour version of this figure can be viewed online.)
surface during the growth process.

An analysis of approximately 100 nucleation sites was performed and we find that the greatest number of nucleations occur with some delay. This was done by taking a large area Raman map approximately 0.7 mm² of a sample fully covered in graphene. In Fig. 10 we show a histogram of the nucleation time for this sample as well as the location and size of each crystal prior to the completion of the growth. In this case of a 7 min full coverage growth we found that nucleation rate peaked at approximately 3 min.

The fact that the maximum nucleation rate is delayed suggests that their may be some underlying mechanism for graphene nucleation. The exact mechanism for graphene nucleation is not known but our results are consistent with the possibility of nucleation based on diffusion of impurities to the copper surface.

We can divide the graphene CVD process into three stages. 1: An initial nucleation phase which is time dependent with individual graphene crystals nucleating at different times. 2: A linear growth rate phase where the maximum speed is constant and determined by the gas composition and flow rate. 3: Final phase where growth rate is limited by the free copper surface area.

Using continuous isotope labelling we are able to quantify the results of each growth phase in order to understand nucleation, linear growth and free surface limited growth regimes.

5. Conclusions

To conclude, we have developed a technique, which allows us to image dynamically the growth of graphene mono-crystals in addition for providing a tool to label different parts of the crystal. This imaging technique enables the assessment of the various anisotropic and non-monotonic growth rates responsible for the dendritic and fractal growth of graphene. These graphene mono-crystals grow from nucleation sites, which are typically impurities or deformations in the copper substrate. We observed that the graphene nucleation is time dependent with individual crystals nucleating at different times independent of other factors. Smaller single layer graphene crystals form as a result of delayed nucleation, but the mechanism and growth rate are the same for both smaller and larger crystals. Finally, the dynamic imaging allows us to draw a precise picture of the CVD growth process, including the relevant diffusion area of the adsorbed species responsible for the growth. Moreover, this technique can easily be expanded to other materials whenever source elements with different isotopes are available, as in the case of MoS₂ or h-BN.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.09.034.

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