The origins of friction and the growth of graphene, investigated at the atomic scale

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Chapter 6

Graphene nucleation on Ir(111)

In the process of graphene synthesis, knowledge on the precise conversion of hydrocarbons into graphene is crucial not only for understanding but also for optimizing the synthesis mechanism. Real-time studies focussing on the growth of graphene are required to reveal the critical parameters for the growth of a perfect nanolayer of graphene. In the work reported here, our variable-temperature STM was used to study the evolution of an Ir(111) surface that was exposed to ethylene. While the temperature was increased, the surface was followed at the nanoscale in order to characterize the behaviour and appearance of the deposited hydrocarbons until they converted into graphene. The results show that graphene nucleates from carbon-containing clusters preferably at iridium steps. In spite of the observed graphene formation, we don't observe significant mobility of the primary carbon clusters. This suggests that the required rearrangements of the carbon layer are taking place on an even smaller scale, possibly atom by atom. The majority of the graphene islands is aligned with the substrate very well. Based on the graphene island shapes, we conclude that the smallest stable graphene unit is half of a unit cell of the moiré pattern.

6.1 Experimental approach

As the variable-temperature STM used in this research is capable of following the iridium substrate surface during the full temperature sweep from room temperature up to 1300 K, the conversion of hydrocarbons into graphene can be studied in detail. The experimental data reported in this chapter were all acquired during a similar kind of experiment: first hydrocarbons (ethylene) were deposited at room temperature and subsequently the substrate was heated slowly in ultrahigh vacuum up to 1000 K or higher, while the substrate was scanned by the STM. In this manner, not only the initial and final structures were observed, but also the intermediate stages of carbon clustering and further rearrangements of the deposit. During these studies no additional carbon was added from the gas phase (except for possible deposition from the residual gas, which was at a pressure below 10^{-10} mbar during the high-temperature stage of the experiment). Further relevant experimental details are provided at the beginning of the following sections.

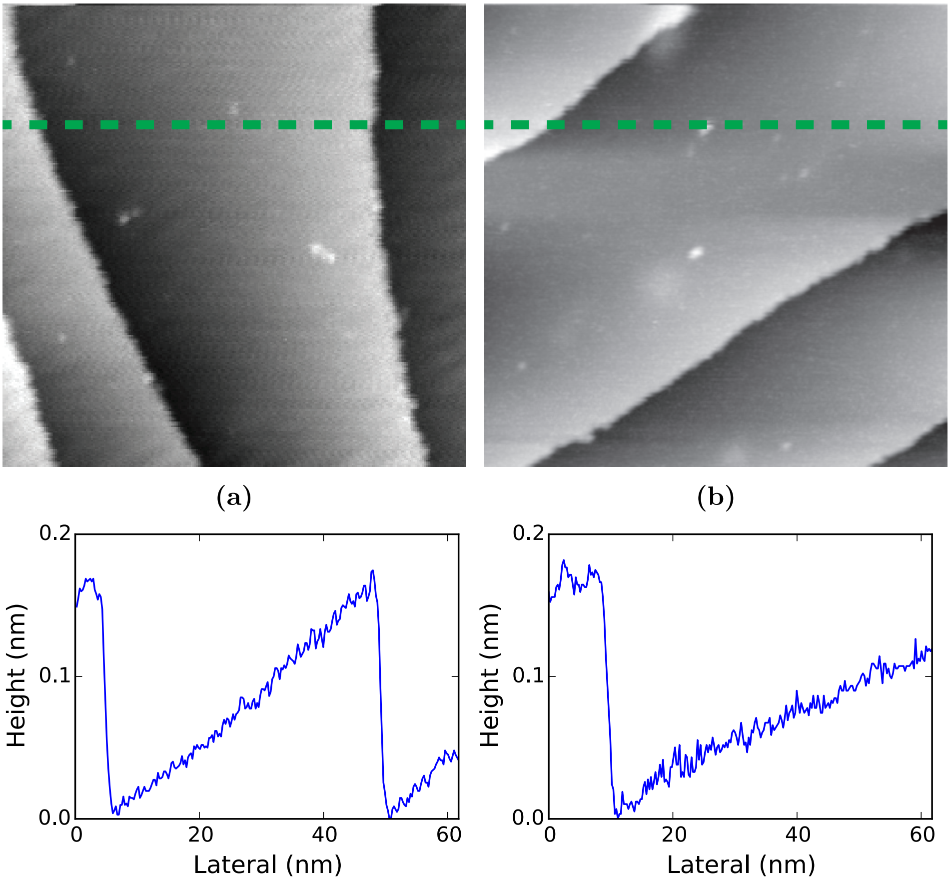
6.2 Deposition of ethylene at room temperature

In this section the behaviour of ethylene on iridium at room temperature is studied. We pay attention to the possibility of clustering of the ethylene molecules or other rearrangements, since these might be relevant for the nucleation of graphene, at higher temperatures.

After sputtering and annealing, the cleaned iridium surface was inspected by STM. After this characterisation, the surface was exposed to approximately 0.5 L of ethylene gas (1.0×10^{-8} mbar during 50 sec), while the STM tip was retracted (to prevent tip effects). Next, the substrate was studied by STM to analyse the ethylene-on-iridium system at room temperature.

In Figures 6.1a and 6.1b, STM images of the iridium substrate are presented that were recorded before and after the exposure to ethylene, respectively. From these images, it is clear that the exposure to ethylene has no significant influence on the surface topography. In addition to some residual contaminants, a few broad $5 - 10$ nm-sized protrusions are visible, which are attributed to argon bubbles, as discussed in Section 5.3.2. No decoration of steps or argon bubbles was observed after the surface was exposed to ethylene. Apparently the deposited hydrocarbons do not cluster and they are too mobile to be imaged. A more careful inspection reveals that both the tunnelling current and the height contours on the terraces exhibit an extra component of high-frequency noise, as a result of the exposure to ethylene. This is illustrated by the two height profiles in Figures 6.1c and 6.1d. This behaviour was observed systematically and can be interpreted as the result of mobile structures on the iridium surface that are incidentally 'imaged' when they move precisely underneath the tip.

The tunnelling microscopy results presented here suggest that ethylene deposited at room temperature on Ir(111) results in mobile structures that



(a) **(b)**

(c) **(d)**

Figure 6.1: The Ir(111) surface imaged at room temperature (a) before and (b) after exposure to 0.5 L of ethylene gas at room temperature. Image size $62 \times 62\,\mathrm{nm}^2$, z-scale 0.25 nm. Sample voltages -0.1 and -0.7 V respectively, tunnelling current 0.1 nA. FFT filtering was performed on the data shown in panel (a) in order to remove a low-frequency vibration. Panels (c) and (d) present height profiles taken at the positions indicated by the dashed, green lines in Panels (a) and (b).

move too fast to be observed by STM. No specific decoration of the iridium terrace edges was observed. Our observations are consistent with the XPS data of Lizzit[49] that seemed to indicate that at room temperature, the ethylene-exposed iridium surface is covered with small (chemisorbed) hydrocarbons, containing only a small (one or two) number of carbon atoms. These species do not cluster at room temperature.

6.3 First observation of carbon clusters

After deposition of ethylene, the iridium substrate was heated up slowly while it was scanned by the STM. In this section we report the first observation of cluster formation on the iridium surface during this temperature ramp.

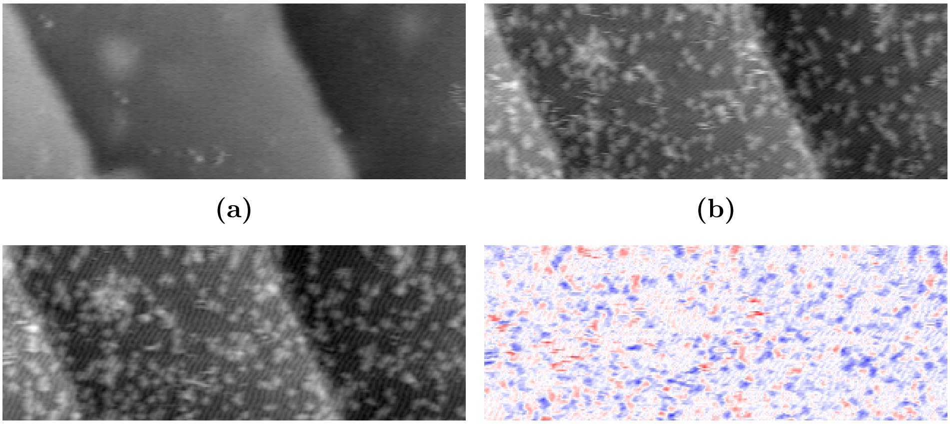
First, the clean iridium substrate was exposed to 3 L of ethylene gas at room temperature. STM images were acquired subsequently, while the iridium substrate was heated at a rate of 0.1 K/sec to a temperature of 800 K. The background pressure was below 1×10^{-10} mbar throughout the entire temperature ramp.

In Figures 6.2a, 6.2b and 6.2c, topographic images of precisely the same area of the iridium surface are shown, recorded at a temperature of 415 K (panel (a)) and 458 K (panels (b) and (c)). Up to a temperature of 415 K, the observed surface is similar to the situation at room temperature (c.f. Figure 6.1b). Apart from the height noise that was discussed already, the images contain no signs of adsorbates on either the terraces or the steps.

At a temperature of 458 K, the entire iridium surface was covered with small, nanometer-sized clusters that each consisted of a small number of sub-units (see Figure 6.2b). As the surface had been exposed to ethylene at room temperature and the pressure in the vacuum chamber remained in the 10^{-11} mbar regime throughout the entire temperature ramp, these clusters can only originate from the hydrocarbons present on the iridium surface due to the ethylene exposure. The clusters were distributed uniformly over the entire surface, indicating that the nucleation of these clusters is not taking place on ‘special’ sites on the iridium surface, such as steps, kinks or point defects on the terraces.

An analysis of the height of the adsorbates shows that the particles have a typical height of 0.12 ± 0.01 nm. This uniformity suggests that most of the clusters consist of sub-units that have an identical internal structure.

In order to explore whether the cluster configuration was stationary, we compare two subsequent STM images. Figure 6.2c shows the same region on the iridium surface as recorded in Figure 6.2b, 9 sec earlier. These two



(a) **(b)**

(c) **(d)**

Figure 6.2: (a), (b) and (c): STM topography images of precisely the same iridium surface, recorded at elevated temperature after deposition of 3 L ethylene at room temperature. The temperature during the image acquisition was 415 K for image (a) and 458 K for both images (b) and (c). The images (b) and (c) were recorded subsequently with a frame acquisition time of 9 sec/frame. Image size $77 \times 29\,\mathrm{nm}^2$, z-scale 0.52 nm, sample voltage -0.74 V, tunnelling current 0.1 nA. Figure 6.2d: result of subtraction of image (c) from image (b). The blue colour indicates added, the red coller removed material; colour scale (blue-white-red): 0.52 nm.

images are aligned and subtracted from each other using the procedure reported in Appendix C. The result is shown in Figure 6.2d, where the blue areas indicate a positive height change and the red areas a negative change. The colour scale (from full red to full blue) is the same as that for the grey scale of Figures 6.2a, 6.2b and 6.2c, namely 0.52 nm. The resulting map clearly indicates that a significant fraction of the small clusters has changed, indicating that the cluster configuration was dynamic on the timescale of 9 sec, at this temperature. In spite of the mobility that is revealed by Figure 6.2d, the clusters clearly do not merge beyond the level of Figures 6.2b and 6.2c at this temperature. The typical length scales of the observed configurations did not evolve beyond 2 nm. This behaviour suggests that the clusters and their sub-units do not yet have the structure and composition of graphene, but that they rather form diffusion-limited aggregates of molecules that still contain a high concentration of hydrogen.

Summarizing, when the ethylene-exposed iridium surface is warmed up above room temperature, we observe clustering of the deposit at temperatures between 415 and 458 K. We interpret these clusters as aggregates of small hydrocarbon molecules, presumably ethynyl. Even though these molecules are somewhat mobile, they do not merge into larger molecules or into graphene at this temperature.

6.4 Conversion from hydrocarbons to amorphous carbon

In this section we concentrate on the final rearrangements in the overlayer, prior to the formation of graphene. This covers STM observations in the temperature range from 458 to 865 K. The STM image acquisition rate was set to 9 sec per image in the temperature window up to 800 K. Above this temperature, the acquisition rate was 17 sec per image. In order to approach the regime of graphene formation slowly, the temperature ramp was kept at 0.1 K/sec. During the full high-temperature experiment, the background pressure remained below 10^{-10} mbar, which ensured that no significant amount of carbon was added during the experiment.

The mobility of the adsorbates was followed during the entire temperature ramp. At a temperature of 760 K, the images indicate that the clusters were no longer mobile, as can be seen in Figure 6.3. As done for the data shown in the previous section (see Figure 6.2), two subsequent STM images were subtracted from each other. At the same timescale of 9 sec, almost no change of the surface was found. This disappearance of mobility of the adsorbates at a higher temperature of 760 K is attributed to a change in

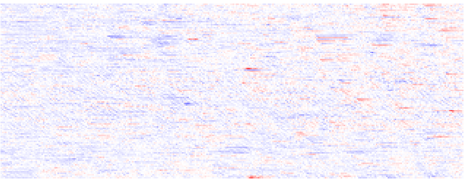


Figure 6.3: Result of the subtraction of two subsequent STM images (time difference of 9 sec) recorded in the same experiment as in Figure 6.2, at a temperature of 760 K. The blue colour indicates added, the red coller removed material; the z-scale (red-white-blue) is 0.52 nm. Image size $77 \times 29\,\mathrm{nm}^2$. The STM images were recorded with a sample votlage of −0.74 V, a high frequency noise component was removed by FFT filtering.

the internal structure of the adsorbates.

A more detailed investigation of the surface was performed at a temperature of 865 K. The STM snapshot presented in Figure 6.4 shows that at that temperature the iridium surface is still covered with a high density of small particles. At this temperature, the clusters do not have one specific height. They are still uniformly distributed and do not cluster significantly. It can be observed that a significant fraction of the step is decorated with particles, although no clear depletion of particles close to the iridium steps is present.

Also at a temperature of 865 K, the mobility of the visible adsorbates was inspected by subtracting two STM images of the same area taken at different times. A set of STM observations is presented in the two upper panels of Figure 6.5. These two observations were done with a 53 sec time period in between. The difference between these two images is shown in Figure 6.5. A clear signal in the differential data is to be expected in case carbon species have moved or disappeared within a timescale of 53 sec. As can be concluded from the two images and from the difference map, the changes are very modest. In particular, they are much smaller than the differences observed on a much shorter timescale at a much lower temperature of 458 K (Figure 6.2). From this we conclude that the clusters observed at 865 K must have a different nature, i.e. a different structure and composition, than those found at lower temperatures.

In addition to the subtraction analysis, another observation that gives information on the mobility of surface structures is their distribution over the surface. In Figure 6.4 no clear clustering of particles can be seen except the almost complete decoration of the iridium steps. This observation suggests that the mobile units have a preference to attach to these steps. The

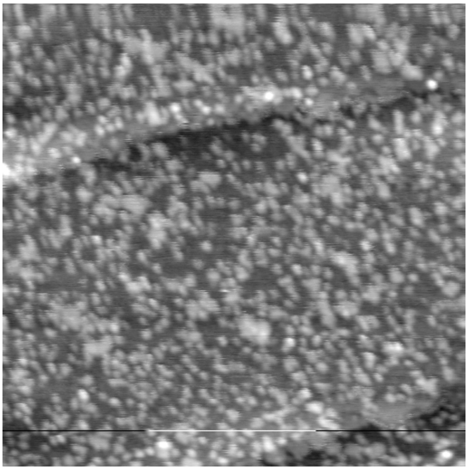


Figure 6.4: STM image of the iridium surface at a temperature of 865 K. Before heating, the surface had been exposed to 3 L of ethylene at room temperature. Image size 125 × 125 nm^2, z-scale 0.35 nm, sample voltage 3.01 V, tunnelling current 0.1 nA.

observation of non-decorated parts of the steps suggest that the mobility has been too low to completely execute this preferential-attachment behaviour. The absence of a depletion of adislands in the vicinity of iridium steps might indicate that the displacement of the adsorbed material has not been diffusion-, but attachment-limited. Note that this should apply to a lower temperature than 865 K, as the clusters observed at 865 K are completely immobile.

It is instructive to view our results in the light of the high-resolution XPS observations of Lizzit et al.[49]. These results indicated that the ethylene-exposed iridium surface forms ethynyl (C_2H) species above 400 K. Additionally, together with other studies focussing on hydrocarbons on Ir(111), they conclude that hydrocarbons are completely dehydrogenated at a temperature of approximately 800 K[72, 73].

Our STM observations do not only agree with the literature, but also provide new insight in the nature of the adsorbates. Based on the XPS data of Lizzit et al., we expect the adsorbates on the iridium surface at a temperature of 458 K to be mainly ethynyl molecules. Our data shows that clusters of these molecules are mobile and do not merge significantly. This behaviour fits to ethynyl molecules as they are individual compounds with saturated bonds. Hence, a chemical driving force for the molecules to cluster strongly is not expected to dominate.

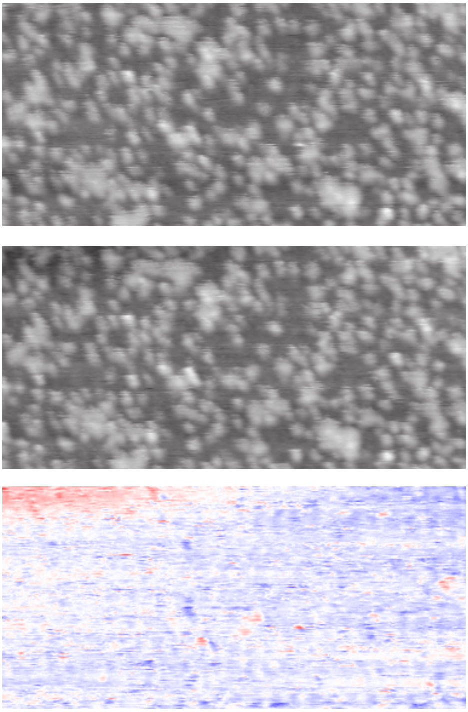


Figure 6.5: Two STM images recorded at the same position on the iridium surface at the same temperature of 865 K with a time period of 53 sec in between. The particles on the surface originate from room-temperature deposited ethylene. The third panel shows the result of image subtraction of the upper two snapshots. Image size 95 × 45 nm^2, z-scale 0.35 nm, sample voltage 3.01 V, tunnelling current 0.1 nA. In the lower panel, the blue colour indicates added, the red colour removed material; the z-scale (red-white-blue) is 0.35 nm.

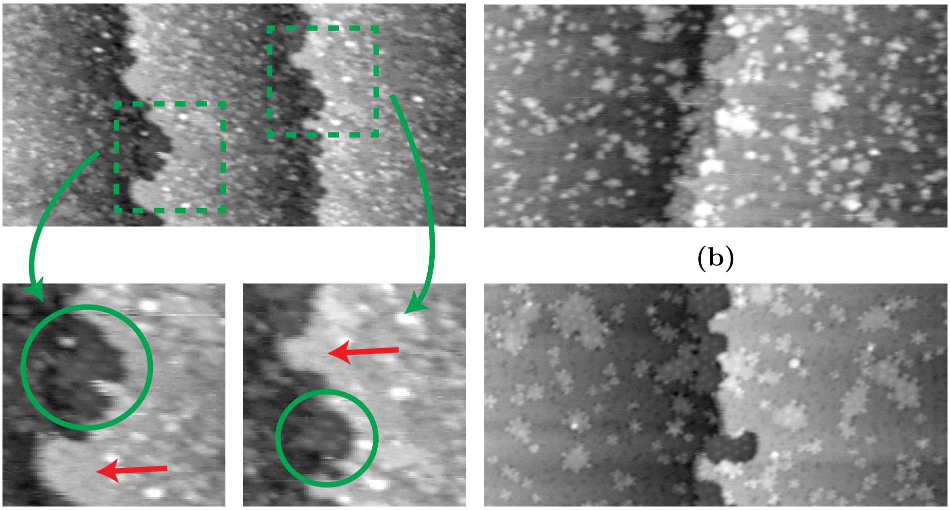
In addition, the data we present here, shows that at a sufficiently high temperature of 760 K, the clusters have lost their mobility nearly completely. Correspondingly, the data of refs. [49, 72] and [73] seem to indicate that at that temperature all carbon atoms are completely dehydrogenated and only amorphous carbon compounds are present at the iridium surface.

Summarizing, our results demonstrate that the evolution of the overlayer slows down nearly completely between 458 and 865 K, in spite of the increase in temperature. This is accompanied by a widening of the distribution of heights of the clusters. These observations suggest very strongly that in this temperature interval the composition of the clusters is changing. This conclusion is supported by the high-temperature XPS data of ref. [49] that indicate that at 865 K the overlayer is completely dehydrogenated. We propose that the high-temperature clusters consist of amorphous carbon. We ascribe the reduction in mobility to the increase in interaction between the clusters and the substrate, when the clusters lose their hydrogen.

In the light of high-quality graphene growth, the observed situation on the iridium surface at a temperature of 865 K is not very positive. In case the observed high density of small clusters does not evolve to a few large clusters, and in case the graphene into which the observed clusters might convert does not have a uniform orientation, the resulting graphene overlayer will contain a high density of domain boundaries. Instead of room-temperature exposure of the iridium surface to ethylene, high-temperature deposition of hydrocarbons might result in higher-quality graphene. This procedure was suggested already by previous studies of graphene on rhodium, performed in our research group[46].

6.5 Lowest temperature of graphene nucleation

The first conversion events from carbon clusters into graphene islands on iridium was followed in *real time* by STM while the substrate temperature was increased slowly (< 0.1 K/sec) from 865 to 1001 K. The slow temperature ramp allowed us to study both the lowest graphene nucleation temperature and the kinetics involved. The design of our STM is such that even over the enormous temperature ramp, the surface could be imaged continuously without interruption. However, residual drift especially in the lateral direction still does have a minimal distortional effect on the imaging quality, e.g. causing straight steps to show up curved in the image and circular islands to show up as curved ellipses. As this lateral drift changes on the timescale of seconds, it makes both a detailed, quantitative analysis of individual images and an analysis by comparing several images recorded



(b)

(a)

(c)

Figure 6.6: STM images of iridium recorded at (a) 967 K, (b) 995 K and (c) 1001 K, after exposure to 3 L of ethylene at room temperature. Two close-ups of the first image are presented to highlight the moiré patterns present (green circles) and to indicate areas without clusters at the iridium steps (red arrows). Image size $125 \times 60\,\text{nm}^2$, z-scale 0.26 nm, sample voltage 3.06 V for images (a) and (b), 2.73 V for image (c), tunnelling current 0.1 nA.

during a temperature ramp rather complicated. Nevertheless, as drift in the z-direction can be corrected using line-by-line linear background subtraction and the iridium surface can be used as a reference, we can perform detailed data analysis based on the recorded heights of the clusters on top of the iridium.

In the following paragraphs, the conversion of the clusters into graphene is discussed based on the observations made by our STM. The structure of the discussion is based on the temperatures at which clear changes in the adsorbates were observed.

$T = 967\,\mathbf{K}$ Figure 6.6a presents the situation at the iridium surface at a temperature of 967 K. Although the image contains some in-plane drift, clear structure changes with respect to the observation at $T = 865\,\text{K}$ can be noticed. These changes are concentrated at the iridium steps. In order to help the reader, two areas are magnified and presented in Figure 6.6a. Two cases are highlighted in these panels: the red arrows indicate protruding

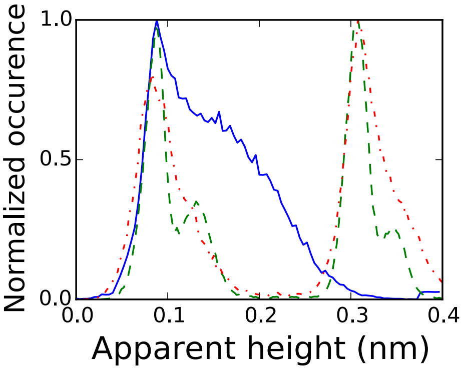


Figure 6.7: Distributions of the apparent heights of the STM images recorded at different temperatures. The blue, solid line corresponds to the STM image shown in Figure 6.5 (upper panel), recorded at a temperature of 865 K. The red, dash-dotted curve represents the data of the STM image shown in Figure 6.6a recorded at a temperature of 967 K and the green, dashed curve corresponds to the STM image presented in Figure 6.6c, recorded at a temperature of 1001 K. The data was corrected by a local plane fit in order to level the terraces.

iridium steps that do not have carbon clusters on top; the green circles indicate patches attached to the lower side of a step with a clear moiré pattern. The presence of the moiré pattern in a patch is direct evidence that the deposit has adopted the structure of graphene: the pattern is a result of the two incommensurate hexagonal lattices of iridium and graphene on top of each other. This gives direct evidence for the presence of the first graphene nuclei to have formed at or below a temperature of 967 K.

In order to characterize the clusters more, a distribution of the heights measured by the STM is presented in Figure 6.7. In this graph, the red dotted curve represents the distribution of the apparent heights of all pixels of the image shown in Figure 6.6a. For comparison, the distribution belonging to the observation recorded at a temperature of 865 K (see the upper panel of Figure 6.5) is shown by the blue, solid line. As the bias voltage of those two observations differs by merely 0.05 V, we attribute the change in the width of the distribution of heights to a change in composition of a significant fraction of the clusters present on the iridium surface. In spite of this change in the distribution, it is not possible to characterize the clusters present at the surface by a specific apparent height. Nevertheless, the upper limit of this height has reduced from 0.2 ± 0.02 nm to 0.06 ± 0.02 nm.

$T = 995$ K A further increase of the temperature up to 995 K leads to evident changes at the steps, as can be seen in Figure 6.6b. The elapsed time between the data presented in the Figures 6.6a and 6.6b is 929 sec. A first, remarkable change is that almost the complete iridium step is decorated with a rim of material. Closer inspection shows that this material exhibits moiré patterns, which indicates that this material is graphene. Second, even though the rim clearly indicates that carbon has accumulated near the iridium steps, we observe no depletion of the clusters on the terraces near the steps. This proves that the carbon material that has been added to the graphene at the iridium steps originates not only from the nearby carbon islands, but from all over the iridium terrace. From this, we can conclude that the redistribution of carbon must rather be an attachment-limited process[74].

$T = 1001$ K After a modest, further temperature increase to 1001 K and a relatively long waiting time of 2079 sec after the last image recorded at 995 K, the appearance of the carbon patches has changed significantly as can be seen in the STM-image in Figure 6.6c. In this image, almost all clusters that lie on the substrate have acquired an identical edge structure and most of the smaller islands have adopted a triangular or hexagonal shape. Also, almost all larger clusters exhibit a clear moiré pattern.

The distribution of heights of the STM image shows a remarkable change, as can be clearly observed in Figure 6.7. The red, dash-dotted curve represents the heights observed in Figure 6.6c. At each terrace, the distribution has split into two peaks, one corresponding to the iridium terrace, and the other to the clusters present at the terrace. Apparently the height of all clusters has become identical, namely 0.045 ± 0.005 nm, which suggests that they consist out of one specific structure. These observations indicate that at a temperature close to 1000 K all carbon clusters have transformed into well-defined graphene patches, some of which form extended rims along steps on the iridium surface. In the next chapters we will inspect the properties of the graphene that is forming on the iridium substrate, such as its mobility and its island size distribution. Here we concentrate further on the nucleation stage.

The observations presented in Figure 6.6 show a clear preference of graphene to nucleate at a substrate step prior to forming out of carbon clusters on the iridium terrace. This preference can be explained in two ways: first, the carbon atom concentration at steps is higher because of the reduced coordination of atoms at a step, which directly results in a reduction of the free energy of the atoms that get trapped at such a step.

Second, the iridium step might act as a template (in the in-plane direction) for graphene nucleation. The first effect increases the attempt frequency of carbon atoms to nucleate into graphene. The second effect reduces the barrier to form a graphene island at an iridium step with respect to the formation of an island on a terrace.

The absence of a depletion zone of carbon close to the graphene-decorated iridium step shows that there is a net transport of carbon atoms to the iridium step from all over the terrace. This behaviour indicates that the growth of the graphene islands is not limited by carbon diffusion over the terraces, but by the rate of carbon atoms/building units attaching to the graphene. Further investigation of the diffusion and attachment of carbon units in the graphene-iridium system is discussed in Chapter 8.

6.5.1 Analysis - graphene nucleation at terraces

In the previous section, the observation by STM of the conversion of carbon clusters into graphene was presented. Most of the data was discussed in qualitative terms and the discussion was focussed mainly on the iridium steps. But evidently, in addition to the carbon at the steps, the clusters on the iridium terraces have changed into graphene also. To obtain quantitative insight in the evolution of all the carbon clusters present, the STM data was processed by the island-extract algorithm described in Appendix D. The resulting 'image mask' was used to obtain the radius and the average height of each island. As all islands have different, complicated shapes, the radius is calculated by first measuring the island area, A, and applying the relation $A = \pi r^2$ (the islands are treated like perfect circles). In this way a 'nominal' radius can be estimated. Figure 6.8 presents the average heights of the islands as a function of their radius and a histogram of the island radii, for all three STM images shown in Figure 6.6. The vertical dashed lines indicate the average island radii.

The statistical analysis of the island evolution quantifies the increase in average island size and provides useful additional insight, for example via the statistical variance of the measured heights. The distributions in Figure 6.8 confirm the qualitative observation of the increase in island size with temperature. This is evident from the increase in average island size (note the vertical dashed lines). It is also reflected in the histograms that show a reduction in the number of small islands combined with an increase in the number of larger islands at higher temperatures (995 and 1001 K). Both aspects are a direct consequence of the ripening mechanism that is at work. This will be discussed in Chapter 8.

Let us now turn to the statistical variance in the observed heights of

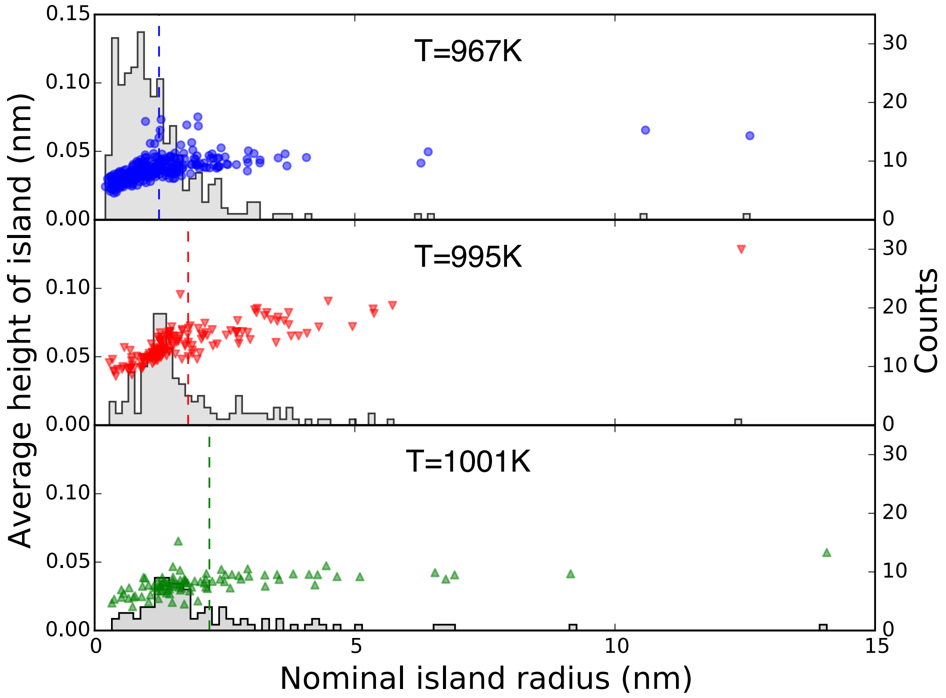


Figure 6.8: Observed distribution of nominal radii (histograms) and heights (symbols) of the islands in the STM images of Figure 6.6 at 967 K (top panel), 995 K (middle panel) and 1001 K (bottom panel). At each temperature, the dashed vertical line indicates the average island radius. The nominal radius of each island was obtained from the island's area, assuming a perfectly circular shape. The island area was obtained by use of the island-extraction algorithm, described in Appendix D.

the islands. In Figure 6.8, we see that the measured height values exhibit significantly less statistical scatter at a temperature of 995 K than at 967 K. The scatter is reduced even further at 1001 K. At each of these temperatures, the scatter in the observed heights is well beyond the accuracy of 0.005 nm, with which the island heights are determined from the STM images. The reduction in the height variance suggests that the islands increasingly adopt a single, well-defined structure as the temperature is raised. A straightforward interpretation is that at 1001 K all patches have converted into graphene: as the graphene nanolayer on top of iridium has a well-defined corrugation, the average height of all larger islands should be identical and no scatter should be present. This is precisely what we find in Figure 6.8. Additionally, this interpretation is corroborated by the transformation in the STM images over the temperature range up to 1001 K of all islands into highly uniformly shaped structures. For, as can be observed in Figure 6.8, both the shapes and the corrugations of all island present are identical. Also the changes observed in the high-temperature XPS spectra of Reference [49] that have been interpreted in terms of a significant transition of the character of the carbon-carbon bonds into that of graphene, are supportive of our conclusion.

The analysis of the islands, presented in Figure 6.8 does not only show an increase of the average island size as function of temperature, but also a remarkable levelling of the average height of the larger islands at 1001 K. This behaviour is visible in the green curve of Figure 6.7, where the emergence of a separate peak belonging to the clusters indicates that they exhibit a uniform height of 0.045 ± 0.005 nm. The distribution in Figure 6.8 shows that at a temperature of 1001 K the islands with an island radius larger than 1.5 nm have adopted this height.

6.5.2 Discussion

At $T = 1001$ K, the average height of all islands reaches its maximum value only at an island radius of approximately 1.5 nm, i.e. somewhat beyond the radius of 1.3 nm of the unit cell of the moiré pattern. The smaller islands, with radii between 1.0 and 2.0 nm, are on average lower and exhibit more scatter in their height values than larger islands. The origin of this scatter is revealed, when we look in more detail at islands with sizes of approximately one moiré unit; see e.g. Figure 6.9. In this image, units are visible that have similar, triangular shapes. Also larger structures appear that consist of two such triangular units, that appear to act as the building units of the graphene islands.

The triangular shape and the size regime of many of the smaller is-

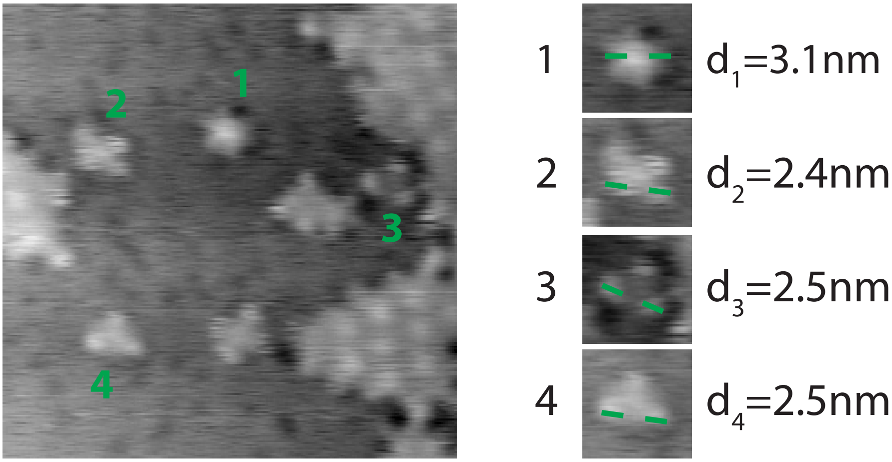


Figure 6.9: STM image of the iridium surface covered with graphene islands, recorded at 1014 K. Some islands are magnified to bring out the differences in orientation with respect to the substrate. Each orientation results in a specific apparent height of the graphene island and in a specific shape of the smallest stable unit of graphene. Image size 30 × 30 nm^2, z-scale 0.13 nm, sample voltage 2.73 V, tunnelling current 0.1 nA.

lands suggest that they are related to the moiré pattern of graphene on iridium(111). Figure 6.9 supports this with measurements of the distances between the corner protrusions of these islands. The corners of islands 2 and 4 in Figure 6.9 are aligned nearly perfectly with the iridium substrate lattice and their distances are 2.5 ± 0.1 nm, in good agreement with the period of the moiré pattern of 2.46 nm. The distances of the corners of island 3 are in agreement with the period of the moiré pattern as well. The shape of island 2 is a rhomb, which is identical to the unit cell of the moiré pattern. Looking at the triangular shape of islands 3 and 4, we suggest that these triangular units are half moiré units and are the smallest stable building blocks of the graphene islands with this orientation. This behaviour is understood better when the registry of graphene on iridium is taken into account. As the influence of the registry is more pronounced during graphene growth, it is discussed in Chapter 7 in more detail. Here, we leave the discussion after noting that the triangular sub-units of the moiré unit cell are assumed to be the part of the unit cell in which the carbon atoms of the graphene align best on the iridium substrate. Island 1 is different. It has a hexagonal shape, has a different orientation and has less pronounced corner protrusions, which makes that its size is more difficult to measure accurately.

As discussed in Section 5.3.5, the orientation and period of the moiré pattern between the graphene overlayer and the iridium substrate depends sensitively on the precise relative orientation of the two lattices. This naturally explains the small differences between the islands in Figure 6.9. For example, islands 2 and 4 are perfectly aligned with the iridium, while island 3 seems to be rotated by 18.5 ± 1.5 degree. We interpret the observed rotation of island 3 as the rotation of its moiré pattern, since the rotation is read off from the positions of the corner maxima, which we associate directly with the moiré pattern. Calculating back from Equation 5.2, a rotation of the moiré pattern by 18.5 degrees should correspond to a physical rotation of the island by 2 degrees. Using Equation 5.3, we find that the period of the moiré pattern should be still almost at its maximum value of 2.46 nm, which is consistent with the distance between the corner maxima of island 3 in Figure 6.9. Island 3 also has a somewhat different apparent height, 20 ± 5 pm instead of 60 ± 10 pm, which fits the description given above. We find that the aligned configuration is the most occurring orientation, which indicates that this is the energetically most favourable orientation, as was observed also in refs [75, 76]. The hexagonal shape of island 1 and its deviating internal structure indicate that the orientation of this island is far from that of islands 2, 3 and 4. We have not observed smaller islands of this orientation, which indicates that the hexagonal structure is the smallest stable structure for this island orientation. It is remarkable that the energy landscape belonging to this other orientation has a dramatic impact on the shape of the smallest, moiré unit sized island.

It might be valuable to note here that the higher parts at the edges of the graphene patches do not have to be those maxima, which are visible in the moiré structure in large graphene islands. The higher parts seem more likely to be electronic edge structures that are related with the growth behaviour of graphene. As mentioned in Section 5.3.4, the non-uniform LDOS affect the height values in our STM data. However, both the shape of the islands and the moiré pattern are still genuine parameters for analysing the islands. Also the analysis of the height data as presented in Figure 6.8 is not deteriorated as this analysis focusses on a relative behaviour of the island height distributions. Further, although the edges of the graphene islands are affected by local changes in the LDOS, these edges still do reflect the moiré periodicity and they can be used to characterize the islands. This will be discussed in more detail in Chapter 7, where the edge behaviour is studied in the light of graphene growth.

The results presented here have remarkable parallels with the work reported by Lacovig and Lizzit [49, 73]. They calculated by DFT, based on high-resolution XPS data, that the transformation from carbon to larger graphene units follows a particular route with intermediate dome-shaped phases with different heights caused by the binding of the graphene to the iridium only at the perimeter. The height of these dome-shaped graphene islands reaches the graphene height of full-coverage graphene already at dome-radii half of the moiré unit radius. Their work fully supports both our observations and our analysis.

Summarizing we conclude that hydrocarbons deposited on Ir(111) at room temperature, start to convert to graphene at 967 K at iridium steps. During this process the carbon concentration at the iridium step increases. Based on the absence of a depleted zone, close to the steps, we conclude that this process is not diffusion limited. At a temperature of 1001 K all carbon clusters both at steps and on the iridium terraces have converted into graphene. The graphene islands show different sizes and rotations on the iridium substrate, however, one orientation is dominating. The minimum size of the islands is, depending on its orientation, half a moiré unit (a triangle) or one complete moiré unit.

6.6 Summarizing conclusions

During the annealing of an iridium (111) surface, after a room temperature exposure to ethylene, we observed several structural rearrangements, before the adsorbate layer is finally converted into graphene at a temperature of 967 K. The real-time observation of the surface with our variable-temperature STM shows that mobile adsorbate clusters formed around 400 K transform into carbon clusters with an extremely low mobility at temperatures up to 967 K. At that temperature, clusters exhibiting moiré patterns appear at iridium steps, indicating the first nucleation of graphene. In spite of the preference of nucleating at steps, no depletion of carbon at the iridium terrace close to the step is observed, indicating that the carbon transport is not diffusion limited. Further annealing to 1001 K leads to an iridium surface only decorated with moiré-pattern containing structures of uniform height, from which we conclude that all carbon has converted into graphene. The increase in temperature also leads to an increase in average island size the graphene clusters. The moiré patterns present in the islands indicate that, at 1001 K, most graphene islands are perfectly aligned with the substrate. Based on the typical shapes of these islands, it can be stated that half moiré units of graphene are the smallest stable configuration of graphene at a temperature close to its nucleation temperature.