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

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### **Citation**

Baarle, D. W. van. (2016, November 29). *The origins of friction and the growth of graphene, investigated at the atomic scale. Casimir PhD Series*. Retrieved from <https://hdl.handle.net/1887/44539>

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**Issue Date:** 2016-11-29

## Chapter 8

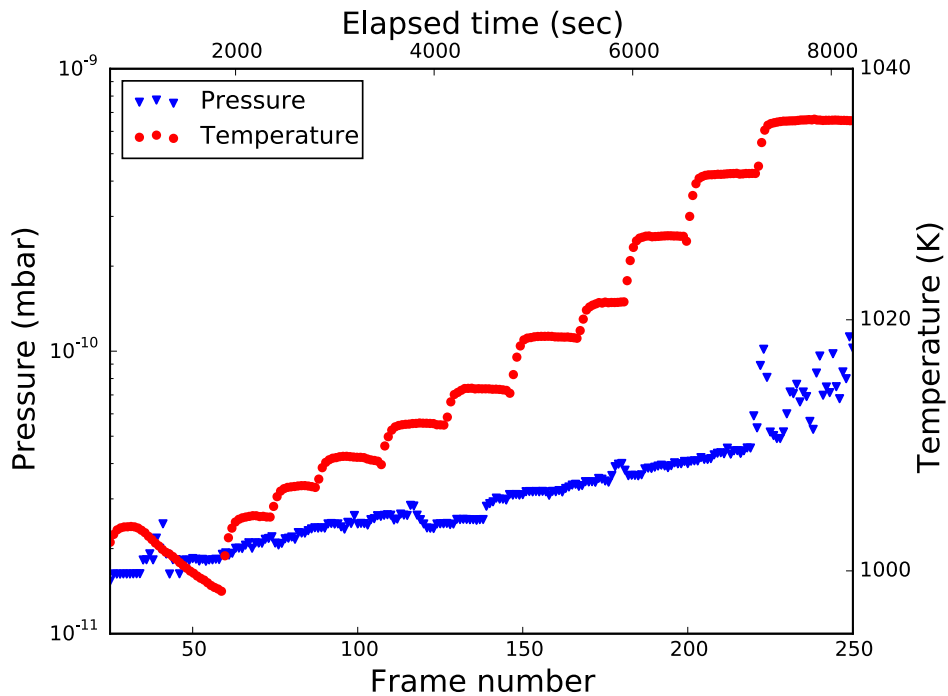
# Graphene ripening: Ostwald beats Smoluchowski

In order to improve the understanding of the growth process of graphene and to control the nucleation density, we studied the ripening of graphene on iridium *in situ*. We investigated the ripening by imaging it with STM, while heating the surface after exposing it to ethylene at room temperature. In this chapter we concentrate on the surface evolution during a slow temperature ramp between 1000 and 1036 K. In this temperature window, we were able to observe the ripening process and to reveal the underlying mechanisms. These mechanisms are expected to have an influence on the final quality of the graphene nanolayer.

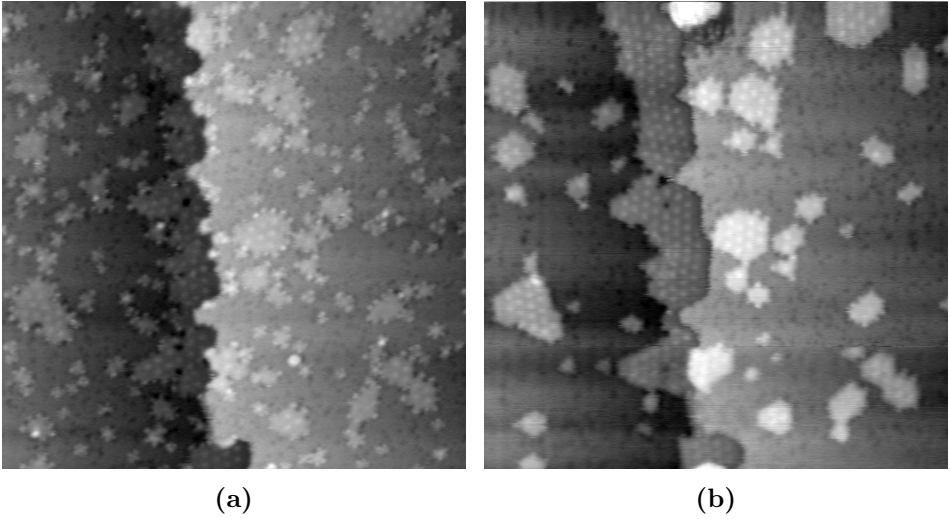
### 8.1 The live observation of graphene ripening by STM

After exposing the surface to 3 L of ethylene at room temperature, the substrate was heated up in vacuum to a temperature of 1000 K at a rate of 7 K/min. Before further ramping the temperature, the system was allowed to equilibrate at 1000 K for a total time of 20 min. Subsequently, a certain surface area was followed by STM for a long period of 1 hour 54 minutes and 24 seconds, while the temperature was increased to 1036 K. The background pressure remained below  $1 \times 10^{-10}$  mbar during the STM imaging. The measured temperature and pressure are presented in Figure 8.1.

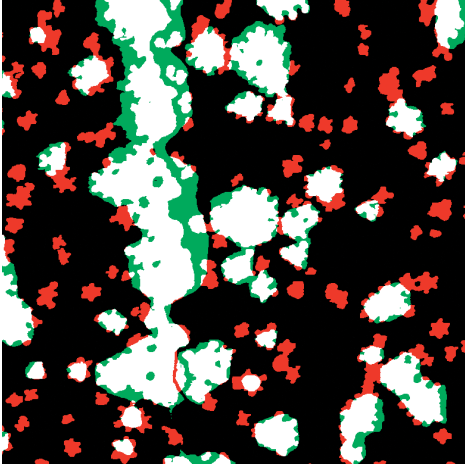
The entire STM image sequence recorded during the experiment can be found as a movie in the electronic Supplementary Material (Movie 1). Two representative frames (frames 42 and 223) are presented in Figure 8.2. During the entire image sequence, an iridium step was kept in view while



**Figure 8.1:** Measured pressure and temperature during the experiment. The reader is reminded that the pressure is not corrected and the temperature is measured via a thermocouple welded on the substrate surface. For clarity, both the elapsed time and the STM frame number are shown on the x-axes.



**Figure 8.2:** Two frames (frames 42 and 223) from an image sequence recorded by STM in which the evolution of graphene islands on Ir(111) was followed while the temperature was increased from 1000 to 1036 K. The images presented here are recorded at a temperature of 1001 and 1036 K respectively. The background pressure remained below  $1 \times 10^{-10}$  mbar during the entire experiment (see Figure 8.1). Image size  $106 \times 107 \text{ nm}^2$ , z-scale 0.26 nm, sample voltage 2.73 V, tunnelling current 0.1 nA.



**Figure 8.3:** Result of subtraction of two frames taken from the STM sequence, frames 50 and 240. For this subtraction, the individual images were first processed to extract the graphene islands and subsequently to convert each of them into a black-and-white image (see Appendix D for details). The white colour in the subtracted image, shown here, presents graphene that was present in both frames; the red colour indicates graphene that was removed between frames 50 and 240; the green colour indicates graphene that was added between frames 50 and 240; the black area indicates iridium that was uncovered in both frames. Image information: The two frames were recorded at temperatures of 1000 K and 1036 K respectively. The time elapsed between the recording of the images was 6303 sec. Image size  $71 \times 71 \text{ nm}^2$ , sample voltage 2.73 V, tunnelling current 0.1 nA.

the temperature was increased slowly.

To illustrate the evolution of the surface during this experiment, two STM images recorded at the beginning (Frame 50) and at the end of the experiment (Frame 240) were thresholded, aligned and subtracted from each other (see Appendix D for the island extraction algorithm). The result is shown in Figure 8.3. In this image, the red areas depict the graphene that has disappeared and the green areas the graphene that has appeared during the observation. The graphene coverages in these images are  $31 \pm 1$  and  $29 \pm 1$  % respectively, showing that within the error margin the amount of carbon has not changed during the experiment.

## 8.2 Discussion

**Smallest islands disappear** At first glance the effect of the slow temperature rise is most evident: all small graphene islands that were present at a temperature of 1000 K are no longer on the surface at 1036 K. Apparently, the smallest graphene nuclei observed at 1000 K are approximately the size of the smallest stable graphene island size at that temperature. At 1036 K, this smallest stable island size has increased and hence the smallest islands present at the lower temperature have become unstable and have disappeared. As a consequence, the average graphene island radius has increased from 1.9 to 3.1 nm. This observation, in combination with an approximately constant graphene coverage, proves that we indeed are in a ripening scenario.

**Unstable islands shrink** The increase of the smallest stable island size of graphene islands implies that at every stage islands should be present that shrink and eventually disappear. Several occurrences of this mechanism are observed in our experiment, as can be seen in Movie 1. These unstable islands produce a net flux of departing carbon. In addition to this shrinking, the larger islands receive a net flux of arriving carbon, leading to a growth of these islands. Both fluxes are balanced, as the graphene coverage remained constant during the experiment. The process of ripening we observed, is known as Ostwald ripening: the smaller, unstable islands decay and the larger, stable islands grow[74, 78, 79].

**No coalescence, no Smoluchowsky ripening** When following the entire image sequence (Movie 1) one observes no mobility of any graphene island. The difference-image presented in Figure 8.3 leads to the same observation: even the smallest graphene islands that have remained on the iridium surface have not moved. From this direct observation it can be concluded that the ripening does not take place via Smoluchowsky ripening, i.e. via the coalescence of entire graphene islands.

This conclusion is in contrast to what is suggested in the graphene growth literature. Based on STM observations performed at room temperature after temperature-programmed growth of graphene on iridium, it was suggested in Reference [47] that the ripening should be of the Smoluchowski type. Our direct observations are incompatible with some of the arguments present in Reference [47], which were based on an indirect measurement of the evolution of graphene islands on the Ir(111) substrate.

In the following paragraphs, the precise ripening mechanism and a detailed energy picture will be constructed based on our STM observations.

**Diffusion of growth units is not limiting** The microscope image presented in Figure 8.2b shows several small graphene islands that have not disappeared yet. As those islands are unstable and hence will shrink, the vicinity of those islands can tell us whether the configuration of the direct surroundings influences these islands. Namely, the local concentration of growth units on the iridium substrate depends a.o. on the curvature of nearby islands and on the competition between the diffusion of growth units over the substrate and the attachment of these units to graphene islands. A relatively low diffusion coefficient results in spatial variations in the concentration of mobile growth units. In such a scenario, a large island (with a large curvature) results in a low local concentration of growth units, hence a small island located close to it will be less stable. On the other hand, similarly, small islands far away from large graphene islands should be more stable.

Inspecting our STM observations with these considerations in mind, we recognise that the smallest islands that are visible in Figure 8.2b are randomly distributed, at locations both close to and far away from the large graphene islands. Apparently, there is no noticeable influence of the presence of large islands and hence we can conclude that the concentration of growth units on the iridium substrate must be nearly uniform, irrespective of the local environment.

In addition to this, when we have a look at the analysis presented in Figure 8.3, we see that the smallest islands that have disappeared (the red-coloured islands) also do not have characteristic surroundings: they are present both close to larger graphene islands and in more dilute areas. All evidence suggests that no direct communication exists between the islands, which leads to the conclusion that the density of the graphene growth units on the bare iridium surface is constant. This insensitivity to the local environment implies that the ripening of graphene is attachment-limited, rather than diffusion-limited. This means that the energy barrier for the attachment of a growth unit to a graphene island is higher than that for the diffusion of the growth unit over the substrate. The attachment being the more difficult step in the ripening process, the two-dimensional ‘gas’ of growth units evens out to a constant background density, from which growth takes place[74, 78, 79]. We can conclude that graphene on iridium evolves via attachment-limited Ostwald ripening.

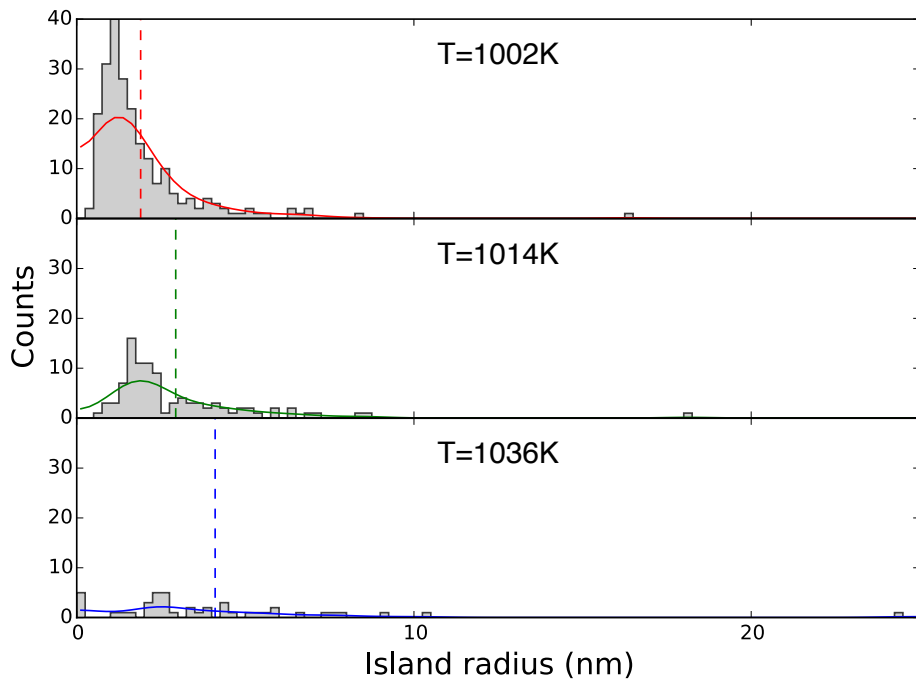
**Ostwald growth and the influence of an iridium step** We inspect Figure 8.3 in more detail in order to distinguish how the ripening has changed the island landscape. First of all, most of the small islands, with



diameters up to 2.5 nm are shown in red, indicating that they have disappeared. Islands that were somewhat larger, up to 4 nm diameter, have survived, but with a reduction in size, as indicated by their edges that have more red than green. Islands larger than 4 nm have grown on average, as their mostly green edges tell. These qualitative observations are in accordance with the Ostwald scenario, which should be accompanied by a well-defined hierarchy of dissolution and growth rates of islands as a function of their sizes, with the radii of the smaller ones shrinking and the radii of the larger ones increasing.

The largest island in the images of Figure 8.2 and in the difference image of Figure 8.3 seems to play a somewhat special role. It does not have a compact shape but is stretched out, so that its radius of curvature is very large. As expected for Ostwald ripening, this island has accumulated the largest quantity of graphene over the duration of the temperature ramp experiment. In addition, this island finds itself in a special location, namely attached to a step on the iridium surface. Figure 8.3 shows that the growth of this island has taken place for a large part on one side, namely the side of the graphene island that faces the iridium step. This is supported by Movie 1. A similar observation of enhanced growth of graphene at a metal step has been reported before, during cooling on graphene on Rh(111)[46], where the incorporation mechanism of the graphene involved fluctuations in position of the metal step. We suggest that the energy barrier for incorporating graphene at a metal step is lower than that at a free graphene edge on the iridium substrate.

**Island size distributions: no diffusion- but attachment-limited ripening** Additional characterization of the ripening of graphene on iridium can be performed using the island size distribution. Island radius distributions extracted from the STM images recorded at different instances (frames 40, 140 and 240) during the ripening experiment are presented in Figure 8.4. At each temperature, in addition to the dashed vertical line that indicates the average island radius, a solid line is shown, which is a guide to the eye for the island radius distribution. This figure shows an overall decrease of the number of islands and an increase of the average island radius as function of temperature; please note that the graphene coverage stayed almost constant during the experiment. More importantly, the island distributions exhibit a significant ‘tail’ to large radii, which might seem more pronounced than expected for Ostwald ripening and might seem to be more fitting for Smoluchowski ripening[80]. However, the distributions that we obtained, can be explained within the framework of Ostwald



**Figure 8.4:** Graphene island radius distributions of STM Frames 40, 140 and 240 (top to bottom) recorded at temperatures of 1002, 1014 and 1036 K respectively. The solid lines are guides to the eye for the distributions and the dashed lines indicate the average island radius.

ripening, when we take into account that the shape of the island size distribution is sensitive to both the coverage of the islands and the detailed growth mechanism. First of all, larger coverages, such as e.g. 10%, are known to result in a tail to larger island sizes[80]. The high graphene coverage in our experiment of approximately 30% should therefore result in a significant tail to larger sizes.

In addition, the distribution of island sizes is influenced by the precise growth mechanism. In case of diffusion-limited growth, less islands with larger island sizes will be observed[80]. Consequently, the island size distribution will exhibit a steep drop just above the most frequently occurring island size. In case of attachment-limited growth, the distribution will fall significantly less rapidly. Our distributions and the analysis based on the direct observation of the ripening both are completely in line with the latter picture that describes an attachment-limited ripening scenario.

### 8.3 Summary and conclusions

The real-time observation of the ripening process of graphene on Ir(111) yielded no signs of any mobility of entire graphene islands. Instead, we observed degradation of smaller islands until they disappeared and growth of larger islands. Our STM observations show that the graphene edges that are directly connected to iridium terrace edges, are preferred growth sites. The spatial distribution of islands on the iridium surface indicates that the density of small, mobile growth units for graphene, is nearly constant over the iridium surface. These findings, in combination with our analysis of the island size distributions at different temperatures, bring us to the conclusion that graphene on iridium ripens via the attachment-limited Ostwald ripening mechanism. We extrapolate our findings by stating that this ripening picture means that, during further growth of graphene by additional carbon deposition at temperatures above 1000 K, nucleation of new graphene islands should not take place.