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

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Chapter 7

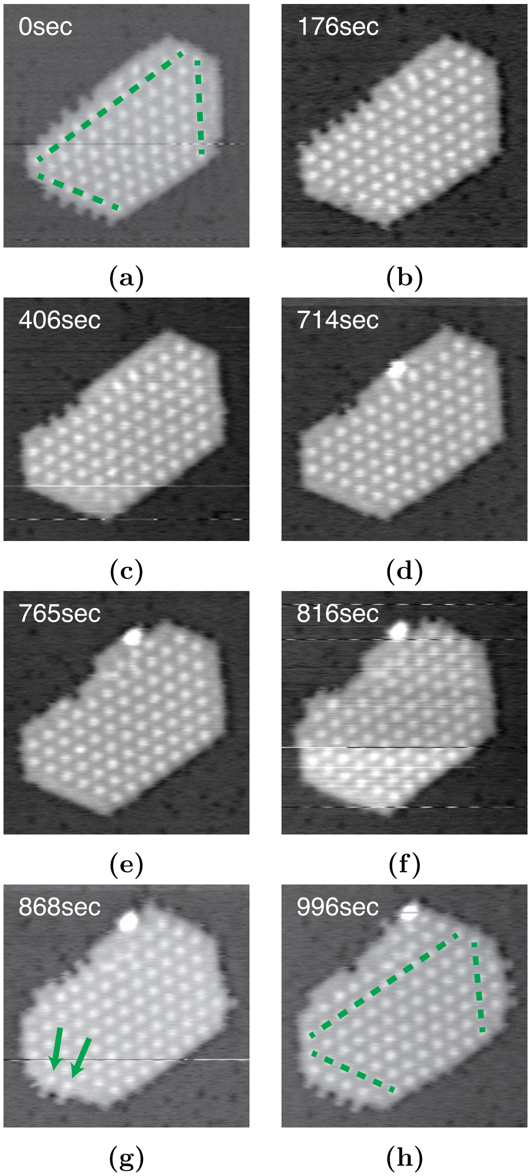
Graphene growth

The growth of graphene is followed at the sub-moiré-unit level, using our variable-temperature STM. At a temperature of 1180 K the growth of graphene on Ir(111) was followed in real time by looking at one graphene island for approximately 1000 sec. The resulting data gives new insight in how new units of graphene are added to the existing island and shows which growth mechanisms are preferred. The alignment and local interaction of graphene with the iridium surface appear to play a decisive role during graphene growth.

7.1 Experimental observation of graphene island evolution

In order to investigate the mechanism of graphene growth on Ir(111) *in situ*, we required a small amount of carbon on the surface. Rather than to deposit this amount explicitly, we made use of the small, residual carbon coverage, below 0.05 ML, that was remaining at the surface after a small number (4) of sputter cleaning and annealing cycles. Subsequently the temperature was raised and, starting from a temperature of 1000 K, the surface was followed by STM continuously while the substrate was slowly heated up to 1300 K with a ramp of approximately 0.05 K/sec. The background pressure in the vacuum chamber remained below 1×10^{-10} mbar at a substrate temperature of 1000 K and increased up to 1×10^{-9} mbar at 1300 K. During the experiment, no gas was introduced in the vacuum chamber.

A sequence of observations capturing the growth process is presented in Figure 7.1. During this sequence, a graphene patch was followed for approximately 1000 sec at a temperature of 1180 K. The temperature was kept constant for this period of time. As no carbon was added during



(a) (b) (c) (d) (e) (f) (g) (h)

Figure 7.1: Image sequence of a graphene island recorded at 1180 K, showing the mechanism of graphene growth. The elepased time relative to the first image is indicated in the top left corner of each image. At the moment these images were recorded, the background pressure was below 1×10^{-10} mbar. Any carbon that attaches to the graphene island is coming either from the residual gas, or from the substrate, or from other graphene islands present at the iridium surface. Image size $36 \times 36\,\mathrm{nm}^2$, z-scale 0.25 nm, sample voltage 3.50 V, tunnelling current 0.1 nA.

this experiment deliberately, all growth observed here must be due either to ripening of the ensemble of graphene patches on the surface or to the attachment of residual carbon, segregating from the interior of the iridium or arriving from the residual gas. This lets the graphene island grow slowly and allows us to investigate the graphene growth mode in detail.

7.1.1 Active edges

A remarkable, first observation from Figure 7.1 is that only 3 out of the 6 edges of the graphene island exhibit growth. These three edges are indicated by dashed, green lines in panels (a) and (h) of Figure 7.1. This results in a reduction of symmetry from the 6-fold symmetry of graphene to a 3-fold symmetric system. The breaking of this symmetry is discussed further in the next section.

The final growth shape of a 3-fold symmetric island should be a triangle. This triangular shape is almost never observed, which suggests that the difference in activation energy for adding graphene is minimal for the two sets of edges. In typical experiments, this small difference in energy will not be observed as the graphene growth is performed relatively fast. Both the details of the growth of the active edges and the graphene registry and edge energies are discussed in the following paragraphs.

7.1.2 Growth mode

The image sequence in Figure 7.1 reveals a non-trivial mechanism of graphene growth. Instead of the growth by kink-creation and -advancement observed in the graphene-rhodium system[77], graphene on iridium seems to grow by first creating ‘fingers’ at the active edge. Subsequently, a stage follows in which the space between these fingers is filled up to finally form a new row of graphene, having the width of one moiré unit.

This growth process is most clearly visible at the lower left edge of the graphene island in Figure 7.1. In the first panel (Figure 7.1a) the entire edge is decorated with ‘fingers’. In the next image, recorded 176 sec later, almost all space between the ‘fingers’ is filled up. However, no moiré pattern is visible in the added graphene. This situation is a rather stable stage, as it takes more than 600 sec before further growth is observed by the appearance of new ‘fingers’. Note, that in the graphene rim at the active edge, the corrugation of the moiré pattern is observed only at the locations where the new ‘fingers’ are present, as indicated by the arrows in Figure 7.1g. On further inspection, we see that the two new maxima of the moiré pattern are already present vaguely in Figure 7.1f, i.e. directly prior to the introduction of the two new ‘fingers’ from there. So, first the moiré pattern is established in the newly added graphene rim, and then the ‘fingers’ appear where the moiré pattern is complete.

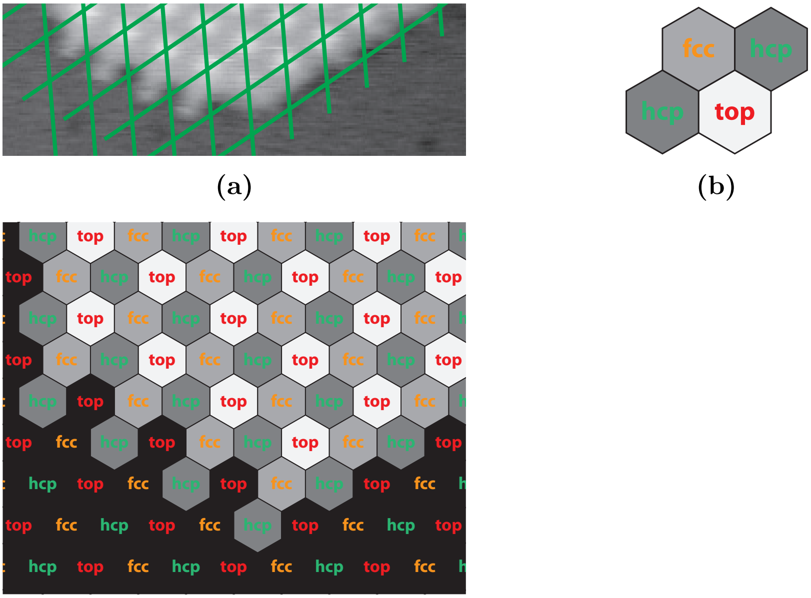
7.2 A geometrical interpretation

The origin of the growth mode and the appearance of the ‘fingers’ is hinted by the precise location where they form. To demonstrate this, a part of the edge of Figure 7.1h is reproduced in Figure 7.2a. The green mash represents the moiré lattice. A quick view at the continuation of this pattern shows that the finger-like protrusions observed during the graphene growth are positioned at specific locations within the moiré unit cell.

Detailed investigation of the behaviour of a graphene layer on iridium has revealed that graphene is physisorbed with a chemical modulation[70], which is a result of the lattice mismatch between graphene and iridium. This mismatch leads to a corrugation that has a maximum distance between graphene and iridium of 0.362 nm at the so-called top locations in the moiré unit cell. A minimum distance of 0.327 nm and hence the strongest interaction between graphene and iridium is realized at the hcp-locations and an intermediate distance of 0.329 nm is found at the fcc-regions. These specific sites are indicated schematically in the moiré unit cell shown in Figure 7.2b.

When we apply this insight to our observed island edges, Figure 7.2a is translated into the schematic picture shown in Figure 7.2c. After this translation, we recognize that all graphene edges are configured such that they are dominated by sites in which the graphene binds most favourably to the iridium substrate. One possible explanation for the specific ‘finger’ configuration is that it enables the edge to maximally postpone the introduction of expensive top-site regions in the graphene. The price that is paid for this is in the extra edge length, which is apparently still lower than the high price that the top-site regions would cost. On the other hand, the mere fact that the top-site regions are not remaining empty within a full graphene overlayer on Ir(111) shows that the edge energy of the complete circumference of a top-site region is energetically more costly than the top-site region itself. An additional contribution to the energy balance could originate from the energetics of hcp- (and fcc-) edges with respect to top-site edges. We speculate that the differences in coordination to the substrate could lead to differences in rebonding of the dangling bonds of carbon atoms at the graphene periphery to nearby substrate atoms.

The STM images presented in Figure 7.1 indicate that after the for-



(a)

(b)

(c)

Figure 7.2: (a) A part of the image of the graphene edge shown in Figure 7.1h. The green mesh is superimposed to emphasise the extension of the moiré pattern at its edges. Image size 27 × 9 nm^2. (b) A schematic representation of a moiré unit cell of graphene on Ir(111). The alignment of the carbon atoms with respect to the iridium lattice is indicated via the 'top'-, 'fcc'- and 'hcp'-labels (see [69] for more details on the labelling). The color of the labels indicates the binding of the graphene with the substrate: the green color stands for a strong binding, the red color for a relatively weak binding and the orange for intermediate binding. (c) A translation of the graphene patch of panel (a) and its edges into the schematic representation presented in panel (b). The preference to have a good alignment and strong interaction at the graphene edge is clearly visible by the presence of 'hcp'-sites at the graphene island edge.

mation of the ‘fingers’ at an active edge, the growth of graphene continues there by filling up the space between the ‘fingers’. The observation of the filled-up configuration for extended periods of time suggests that this configuration is energetically stable or, at least, metastable. Interestingly, in this configuration, the corrugation that is characteristic for the moiré pattern is not yet developed in the section that the filling-up has added to the graphene layer, even though that section seems to be complete and it has the width of a full moiré unit. We speculate that the graphene in the ‘unfavourable’ regions between the locations where the ‘fingers’ were, exploits its own, lateral deformability, to adjust better to the substrate and thereby locally avoid having carbon atoms in top sites. In this process, it is essential that also the edge of the filled-up region is free to deform. It is precisely this freedom that is necessarily sacrificed when that region protrudes to form the next ‘finger’, thus forcing the now enclosed region to reduce its deformation and tolerate a number of carbon atoms in top sites. These are the high carbon atoms that stand out and together form the protrusions in the moiré pattern.

Finally, the schematical representations in Figures 7.2b and 7.2c clarify why the 6-fold symmetric system of one-atomic layers of both graphene and iridium has broken into a 3-fold symmetric system. The two types of edges at the graphene perimeter, characterised by a difference in edge energy, leads to a breaking of the 6-fold symmetry and to a different growth behaviour of these types of edges. In principle, a similar scenario could be envisioned also for the other three edges, with ‘fingers’ growing out and the space in between being filled up in the next stage. But the fcc- and hcp-regions would have to switch roles from one edge type to the other, which, apparently raises the energy barriers for the other edges sufficiently that they don’t exhibit any growth or ‘finger’ formation on the time scale of our experiments.

7.3 Conclusions

We have presented the first observation of the high-temperature growth of graphene in real time at the sub-moiré-unit level. The monitoring of a graphene island by the STM at a temperature of 1180 K, growing from a low flux of carbon atoms, probably originating from segregation of dissolved carbon, enabled us to follow the growth of this island ‘in slow motion’. From the observations it can be concluded that the growth only takes place at three of the six edges of the graphene island, which indicates that the iridium-graphene system exhibits a 3-fold symmetry. The growth is characterised by a two-step process: first the edge is covered with finger-like structures that appear on specific positions with respect to the moiré unit cell. Only at the moment, at which such a 'finger' starts forming at the edge, the corrugation of the moiré structure becomes visible in the moiré unit, to which the finger is attached. In the next step, the space between the fingers is filled up with graphene, however, no moiré corrugation is visible in this new row of graphene units just added.

The observed growth mechanism is explained by the alignment of the graphene lattice with respect to the underlying Ir(111) surface. The local interaction between graphene and the iridium surface atoms plays a decisive role in the growth of graphene. Both the formation of the 'fingers' and the filling up of the regions between them with a graphene layer that initially exhibits no corrugation, are demonstrations of the dominant tendency of the Ir(111)/graphene system to avoid the unfavourable configurations with carbon atoms in top sites with respect to the Ir substrate. This results in peculiar growth dynamics and makes the growth of the two types of graphene edges on Ir(111) strongly non-equivalent.