Formation of graphene and hexagonal boron nitride on Rh(111) studied by in-situ scanning tunneling microscopy

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Citation

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Chapter 13 A universal description of graphene formation on transition metals

In the previous chapters, the interaction between carbon and Rh (Fig. 8.1E) has been described. Based on the experimental observations, we have been able to develop a recipe for obtaining high-quality graphene. In brief, it was found that the growth form (carbide or graphene) obtained by exposure of Rh(111) to a carbon-containing precursor gas is determined by the starting situation in the temperature range of 750 to 1016 K. Exposure to ethylene at temperatures above 1016 K can lead to full coverage of graphene, but also results in a high density of carbon atoms that have dissolved in the Rh substrate before the onset of graphene formation. These dissolved carbon atoms then segregate during cooling and destroy the high-quality graphene structure on top. Our optimized recipe is to

(i) first pre-expose the Rh surface to ethylene at a low temperature, e.g. room temperature;

(ii) heat up the sample, in order to form graphene nuclei;

(iii) expose the sample at elevated temperature to further ethylene at a low pressure, in order to cover the entire surface with graphene.

The rational behind this recipe is provided by the combination of the direct STM observations reported in part II and the considerations published by McCarty *et al.* [53], which can be combined into the following, new physical picture. In Fig. 13.1, the black line represents the density of carbon adatoms on the Rh surface, dictated by equilibrium with carbon dissolved in the bulk. The shape and position of this line is determined by the carbon concentration in the substrate, and by the dissolution energy of carbon [53]. The solid red line represents the carbon adatom density deriving from equilibrium with the graphene islands. The point where the black line crosses the solid red line gives the dissolution temperature of graphene. We now add the solid blue line, which represents the carbon adatom density which would establish equilibrium with the carbide islands. It must be higher than the one for graphene, because a lower dissolution temperature for the carbide, at comparable carbon concentration in the bulk, has been observed. The dashed red and blue lines are the supersaturation necessary for observable nucleation of graphene and carbide. The reason that the dashed blue line (carbide) has been drawn lower than the dashed red (graphene) line is that direct deposition of ethylene between 750 K and 975 K leads to the carbide phase. The physics behind this could be that the critical nucleation size for graphene is larger.

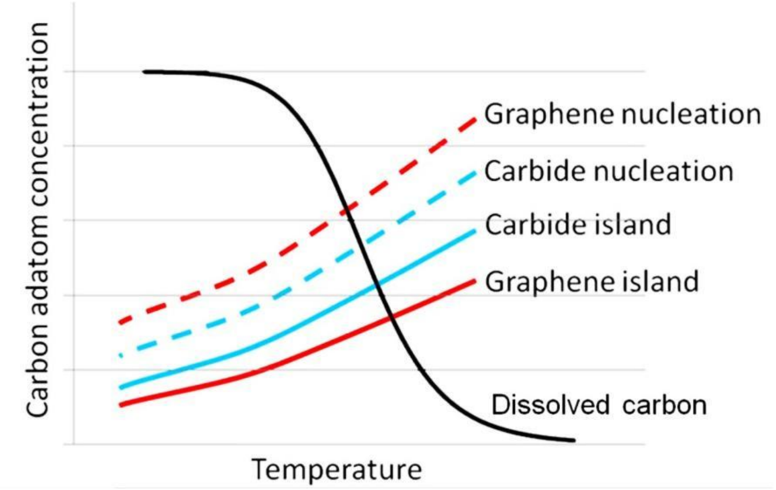

Fig. 13.1 Schematic diagram, showing the temperature dependence of various equilibrium adatom concentrations of carbon on the metal surface. The black line is the carbon adatom concentration, which is in equilibrium with carbon in the bulk. The solid red line is the adatom concentration for equilibrium with graphene islands (after [53]); the solid blue line is the adatom concentration for equilibrium with carbide islands; the locations where the solid lines cross the black line are the dissolution temperatures for graphene and carbide; the dashed red and blue lines indicate the supersaturation levels required for nucleation of graphene and carbide, respectively, on a clean metal surface.

Now let us use this simple picture to explain the complexity of the observed nucleation and growth phenomena. We start by discussing the competition between graphene and carbide formation. In the experiments where the surface is first exposed to ethylene at room temperature and then warmed up, clustering of CH_x must make the surface carbon concentration locally very high, beyond that shown by the dashed blue and red lines. Under such conditions, both carbide and graphene nuclei can be formed. With time, the carbide islands will disappear and the graphene islands will become larger, since they are energetically more favourable. This is also why the carbide may form first on metal surfaces, but after long periods of annealing (e.g., 400 minutes) at high temperature, it can transform to graphene [105]. In addition, ripening [87] is active to make the average size of the graphene islands continue to grow. When ethylene is subsequently deposited onto the seeded surface, as shown in Fig. 8.3, the system is kinetically trapped in a ‘graphene-forming’ mode. Now, graphene islands are already present and only a low carbon adatom density is needed to continue the growth. Because of the low ethylene pressure and the rapid incorporation of the deposited carbon into the graphene matrix, the density of adatoms cannot become high enough for nucleation of carbide (or new graphene islands). So all this taken together resulted in a surface fully covered by graphene.

Now we turn to the role of dissolved carbon atoms. When we exposed a clean Rh(111) substrate directly to ethylene at 1035 K, without the low-temperature seeding step, several dark spots appeared in the STM images, before the graphene was formed (Fig. 13.2A). Graphene formation only started when the ethylene pressure reached 3.5×10^{-7} mbar, which we associate with the dashed red line in Fig. 13.1. In the framework of Fig. 13.1, it is natural to ascribe the dark spots in Fig. 13.2 A to dissolved carbon atoms, because the supersaturation required for graphene nucleation is high enough for noticeable carbon dissolution. This dissolution leads to a relatively high concentration of carbon atoms in the substrate, close to the surface. Since the solubility of carbon in the Rh is a strong function of temperature, there is a strong driving force for the dissolved carbon atoms to segregate during cooling and accumulate between the Rh substrate and the graphene overlayer. The resulting accumulation layer distorted the regular graphene moiré patterns, as shown in the previous chapter. As can be seen in Fig. 13.2B, it was possible to partly re-dissolve these extra carbon atoms by heating the sample to the growth temperature. We speculate that this is only possible as long as the density of carbon in the accumulation layer is not sufficient for the formation of a second layer of graphene. In the latter case, we should have observed the top graphene layer dissolve together with the accumulated (graphene) layer. Note, that the high concentration of dissolved carbon atoms led to a higher dissolution temperature (1118 K) of graphene for this sample, in agreement with our expectation from Fig. 13.1.

Fig. 13.1 shows that in order to have less C dissolved during the direct deposition, one should use a higher pressure. The argument for this counterintuitive approach is that by increasing the pressure the nucleation rate increases super-linearly, whereas the rate of dissolution will simply be proportional to the pressure. Following this idea, we have been able to improve the quality of the graphene overlayer on Rh as is demonstrated in Fig. 13.2C. The temperature of the clean Rh sample was first raised to 1028 K, after which the ethylene pressure was quickly increased to a high value of 3.9×10^{-6} mbar. The graphene layer that formed under these conditions covered the whole surface with a much lower defect density than the graphene structure shown in Fig. 8.2C. However, in spite of the high ethylene pressure used here, the moiré pattern still distorted due to segregated C when the sample was cooled to room temperature (Fig. 8.2D). The combination of the high solubility of C in Rh and the macroscopic thickness of our substrate (1 mm) made it practically impossible to completely avoid C dissolution at high temperatures and segregation of dissolved C during the cool-down.

One of the recipes reported for a single monolayer of graphene on Rh(111) is to expose the clean rhodium surface for 3 minutes to 2×10^{-7} mbar ethylene at an even higher temperature of 1100 K [89]. We have monitored this recipe with our STM at this high temperature, but graphene was not formed under these conditions and also not with longer exploring times up to 10 minutes. Instead, our images show that in this case a graphene layer was formed only after the exposure, during cooling of the sample, when the temperature had reduced to ~1000 K, showing that, in this recipe, the graphene film is assembled completely from segregated C. The STM images at room temperature did not show distortions, in accordance with the images in Wang et al. [89]. We attribute this absence of distortions to a nearly complete consumption of the dissolved C in the near-surface region by the graphene monolayer. The difficulty in this procedure is to precisely control the coverage, i.e., the total amount of segregated C. It is relatively easy to obtain large areas covered by graphene suitable for STM imaging or for a local spectroscopic measurement. But it is very difficult to reach full coverage of the surface with graphene of precisely one layer thickness, i.e., without any excess C.

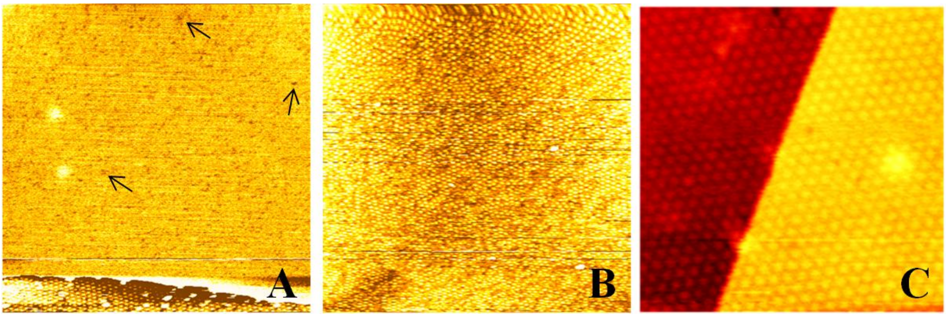

Fig. 13.2 (A) STM image before the whole surface was covered by graphene. Some dark points (indicated by the arrows), which can be caused by dissolved carbon, are visible. The temperature of the sample was 1035 K and the pressure of ethylene was 3.5 x 10^{-7} mbar. (B) STM image taken at 1025 K after the graphene-covered sample was cooled to room temperature and heated up again. The regular moiré structure partly reappeared during heating, after it had become distorted when the sample had been cooled to room temperature. (C) STM image of graphene-covered Rh, which was achieved by direct ethylene deposition and imaging at 1028 K. The pressure of ethylene was quickly raised to 3.9 x 10^{-6} mbar.
The image size is 170 x 170 nm^2 for A and B, and 65×65 nm^2 for C.

How to control the thickness of the graphene, in particular how to avoid the nucleation of the second layer below the first layer, now seems evident: after the (first) graphene layer has been formed on the metal surface, the nucleation of a second layer can be avoided by cooling down the sample very rapidly. Also by choosing a metal with a low solubility for C, for example, Cu, nucleation of the second layer can be further suppressed. The two-step recipe, first nucleation and then growth, can be used to trap the system into a state with a lower amount of dissolved C in the metal substrate as demonstrated in section 8.3. This recipe is also useful to arrive at a low growth temperature at which a minimum of C dissolves into the substrate and the graphene overlayer grows with a low strain level. In the case of Rh, this recipe still resulted in a considerable density of translational defects, due to the relatively small domain size, but on other substrates, such as Ni(111), where there is no superstructure [26], we expect that this will not pose a problem.

In conclusion, the schematic diagram in Fig. 13.1 can explain all the experimental results. And it can easily be adapted to other CVD procedures on transition metals. The key elements that may vary from system to system are the stable phases, their formation energies and step energies, the dissolution energy, and the critical nucleation size. It can also explain why the reported recipes are sometimes not very reproducible. For example, the carbon adatom density is a function of the bulk carbon concentration. In a non-equilibrium case, it also depends on the time during which the sample was held at elevated temperature, and the rate of increase or decrease of the temperature. These parameters vary from case to case and are often not specified.

The central message of this chapter is that by following an appropriate reaction path through the diagram in Fig. 13.1 one can control the formation of the three carbon phases: graphene, carbide, and dissolved carbon. Recipes for producing high-quality graphene should not only consider temperature and pressure, but also the initial situation, the rate of temperature increase/decrease, and the bulk carbon concentration.