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

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Chapter 9 Towards the optimal growth recipe

9.1 Introduction

In the previous chapter, it was shown that the deposition of ethylene can be controlled to form exclusively graphene rather than carbide, and to bring the process to a lower temperature. In this chapter we show that as an alternative to direct deposition, also the segregation of dissolved carbon atoms could be used in a controlled way, in order to form graphene. By cooling down the sample very slowly, the effective flux of segregated carbon is kept low. These carbon atoms also tend to follow the structure and orientation of the pre-existing seeds; if these have the graphene structure, this procedure results in the growth of graphene. After the segregation has come to an end, the coverage of the graphene overlayer can be brought to completion by a final ethylene exposure. This lower process temperature will be associated with a lower density of C dissolved in the substrate and, if it is of any importance, also with a lower strain due to the differential thermal expansion between the graphene overlayer and the Rh substrate [91, 92].

9.2 Using segregated carbon to form graphene

This alternative procedure using segregated carbon to form graphene was also successful, as is shown in Fig. 9.1A, where a part of the surface was followed from 862 to 829 K. This is very promising for achieving 2D single crystalline graphene, using

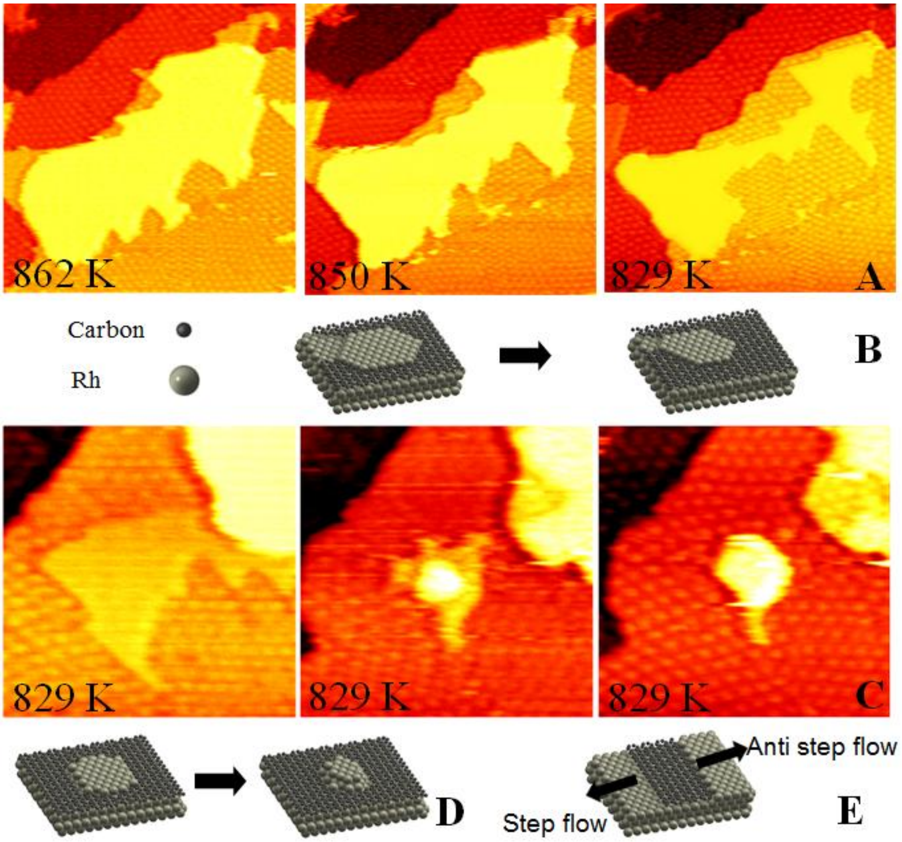

Fig. 9.1 Graphene formation by dissolved carbon and Rh double layer defect formation. (A) STM images of the same area during the cooling down of a Rh sample, partly covered by graphene, after adsorption of ethylene at room temperature and annealing to 977K. The Rh island indicated by the red arrow is in the same atomic level as the graphene indicated by black arrow. They seem to be in different levels because of the sample voltage setting. The segregated carbon followed the orientation of the existing graphene. Image size: 100 × 100 nm^2. (B) A simple atomic model of the graphene formation by segregated carbon. The Rh island became smaller, because Rh diffused away via the small opening in the graphene layer. (C) Graphene growth, by adding more ethylene while the sample was held at 829K. These images show how a Rh island, enclosed by graphene, was pushed into a double layer island with half of the original area. Growth of the graphene stopped after the whole island had become a double layer. Image size: 50 × 50 nm^2. (D) A sketch of the formation of the Rh double layer island. (E) The concept of step flow and anti step flow. In the latter case, Rh atoms have to move to the upper atomic level, in order for the surface to accommodate the additional carbon.

dissolved carbon. One difference, relative to deposited carbon, is that the graphene layer also chose the growth direction (Fig. 9.1E) where the Rh step has to retract, to allow further graphene growth. To emphasize that this proceeds against the direction of regular step-flow growth, we refer to this as ‘anti-step flow’; in some papers it is called ‘growth by etching step edges’ [94]. In this temperature regime, Rh atoms should be expected to diffuse much faster over the surface than the carbon atoms can in graphene. When sites become temporarily available, as a result of step fluctuations of the Rh, newly arriving carbon atoms may fill op the vacant sites, the strong cohesion in the graphene preventing the Rh step from fluctuating completely back to its original shape and location. This anti-step-flow mechanism resulted in a large number of Rh islands enclosed by graphene.

9.3 Further ethylene deposition

Fig. 9.1C shows one of Rh islands enclosed by graphene, to which more ethylene had been added. The carbon introduced by the ethylene deposition was found to also be accommodated via the anti-step-flow mechanism, instead of forming graphene on top of the enclosed Rh. In this stage, Rh atoms were pushed up and nucleated a higher atomic layer; the graphene stopped growing when the complete enclosed Rh island had a double-layer height (Fig. 9.1A). The reason that, in Fig. 9.1A, the Rh did not become a double-layer structure, is that, in that case, there was a narrow passage in the graphene layer, through which the Rh could diffuse away. In separate experiments, in which the Rh was exposed to ethylene at a low temperature of 864 K, the growth of graphene, both at the free edges of graphene islands (‘step-flow’ growth) and growth against the Rh steps (‘anti-step-flow’) was observed. At this temperature, the growth rates for these two mechanisms were comparable. At the higher temperatures of the experiments discussed before, e.g. at 975 K, the anti-step-flow growth rate was much lower than the step-flow growth rate. That the mechanism was still active is illustrated by the appearance of double-layer defects in the final stages of the graphene growth, as is indicated by the two arrows in Fig. 8.3B. The temperature dependence of the ratio between the two growth rates can be explained as follows. Assume that decomposition of ethylene or the growth of graphene has a lower energy barrier at the step edges of Rh than on the terraces. At 864 K, the resulting higher decomposition or growth rate of ethylene at the Rh step makes the amount of carbon atoms available for anti-step-flow higher than that for step-flow growth. At 975 K, all ethylene on the Rh terraces rapidly decomposes, which means that the carbon production rate is not limited, at that temperature, by the decomposition, but by the deposition of ethylene. Since the steps represent a much smaller effective area than the terraces, and the anti-step-flow requires an additional process of moving Rh atoms, the ratio between anti-step-flow and step-flow should become low at high temperatures. Nevertheless, anti-step-flow will still occur, and it will lead to Rh double-layer defects. The only way to reduce their density is by further elevating the temperature or by making the average distance between the graphene nuclei larger than the average distance between the steps on the Rh substrate.

9.4 Conclusion

Our attempts to use segregated C plus further ethylene deposition at low temperature to form a complete, undistorted graphene overlayer were successful. The added graphene follows the graphene phase and orientation of the initially present nuclei. This procedure forms a very promising route for achieving 2D single-crystalline graphene. However, the low growth temperature results in a high growth rate of graphene in the anti-step-flow direction. This results in many Rh double-layer defects, which form holes in the final graphene overlayer.