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

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Chapter 12 The structure of graphene on Rh

12.1 Introduction

It has been proposed that on Ru(0001) graphene is supported by a Ru 'nail' structure, with one nail under each unit cell of the moiré pattern, as sketched in Fig. 12.1 [94]. The nails have a height of one atomic layer of Ru. This support structure enables the graphene to avoid or reduce interaction with the Ru substrate, where the lattice mismatch would make this interaction unfavorable. Not only is this structure of interest in view of the competing interactions that are at play, but also because of the application potential, with this structure serving as a scaffold for the formation of nanopatterns, e.g. regular arrays of metal nanoparticles.

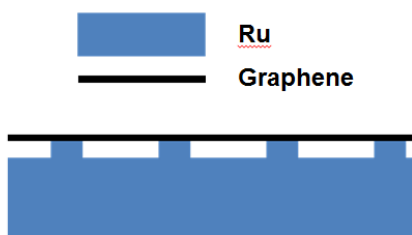


Fig. 12.1 Sketch of the 'nails' under the graphene layer on Ru(0001). Ru forms monolayer high nails on the Ru surface that support the graphene structure and reduce unfavorable interaction between the graphene and the Ru substrate [94].

Our *in-situ* growth movies of graphene on Rh(111), as illustrated by the STM images in Fig. 10.1 and Fig. 10.2, seem to indicate that the graphene layer forms on top of the Rh crystal, without the intervention of a nail structure. Nevertheless, one could still imagine that additional Rh atoms could have crept under the graphene layer to form the nails directly after the graphene had formed. In order to exclude such a scenario, we have performed a separate experiment, which has enabled us to put an upper limit on the amount of Rh incorporated as nails below a graphene island.

12.2 Experiment

The geometry that we have chosen for this experiment is that of a vacancy island in the Rh substrate, partly covered by graphene. In order to create such a geometry, we first bombarded the clean Rh(111) surface by 400eV Ar⁺ ions for 10 minutes at room temperature, and slowly warmed up the sample to 800 K. An STM measurement was performed to monitor the size and density of the vacancies on the sample. If the annealing temperature is too low or the annealing time is too short, the typical size of the vacancy islands will be small, which will result in a larger error margin in this experiment. On the other hand, if the annealing temperature is too high or the time is too long, the vacancy islands will become impractically large for our STM observations. After cooling to room temperature, we exposed the Rh sample with its vacancy islands to 2.5×10^{-7} mbar s of ethylene gas. Again the sample was slowly annealed, this time to 870 K, in order to form graphene islands within the Rh vacancy islands. Then the temperature was reduced to 745 K, to avoid further ripening of the Rh vacancy islands. Fig. 12.2A shows the typical geometry that was obtained by this preparation procedure.

In order to explore the possible presence of Rh atoms that were supporting the graphene in the Rh vacancy islands, we exposed the surface to O₂ at 745 K, thereby removing the graphene layer (Fig. 12.2B-D). It is safe to assume that it is very difficult for Rh adatoms to diffuse out of a vacancy island in the Rh substrate. So, if there were Rh nails under the graphene patch, we should expect to observe a reduction of the area of the Rh vacancy island upon removal of the graphene, when the Rh atoms that were originally in the nails would join the inner edge of the Rh vacancy island.

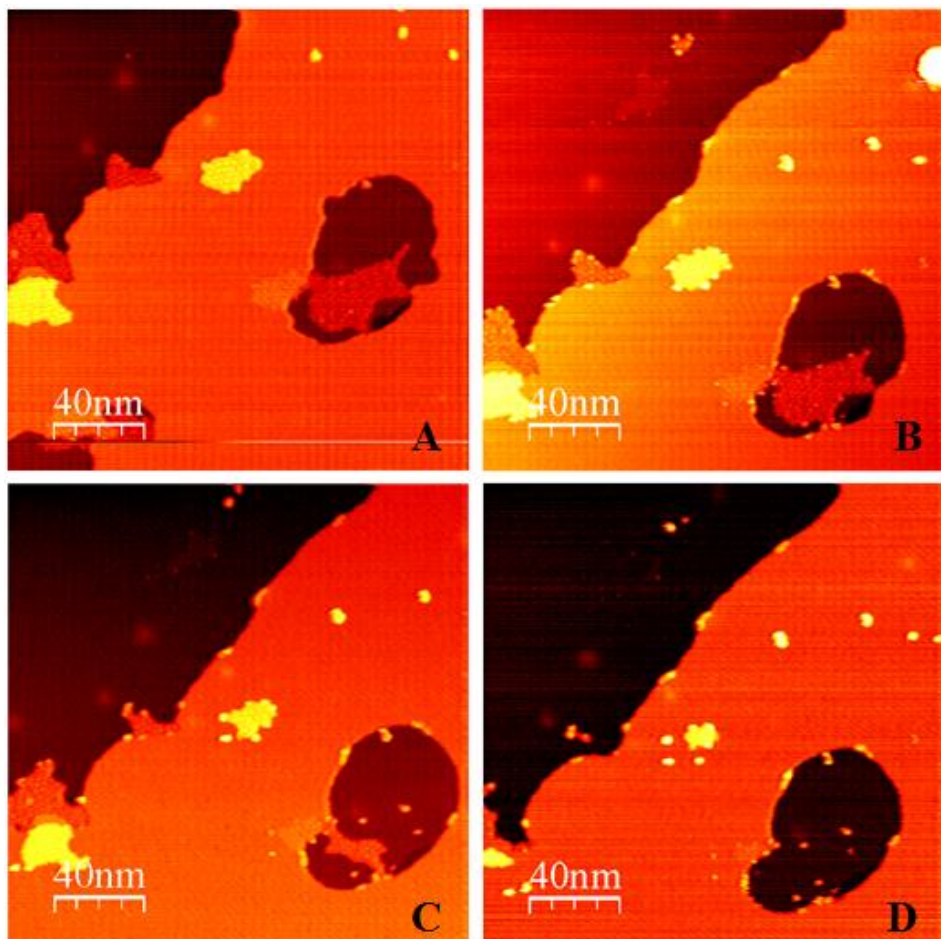


Fig. 12.2 Four snapshots from an STM measurement, in which a Rh vacancy island with a graphene patch inside was exposed to O_2 at 745 K. (A) The initial situation of this structure. (B) 160 Seconds after the start of the exposure part of the graphene island was reacted away. (C) After 251 s, most of the graphene island was removed. (D) Complete removal of the graphene patch was obtained after 319 seconds.

The sizes of all images are $200 \times 200 \text{ nm}^2$; they have been taken at a sample voltage of $V_b = -0.75 \text{ V}$ and a tunneling current of $I_t = 0.05 \text{ nA}$. The frame rate was 22.8 s/frame .

12.3 Result and conclusion

In Fig. 12.3, the development with time of the area of the Rh vacancy island and that of the graphene patch in Fig. 12.2 are shown. Several STM images were measured before and after the oxygenation process, to test for systematic errors, for example, ripening of the Rh island. After O₂ had been admitted into the chamber (the increase of the green line in Fig. 12.3A), the area of graphene reduced to zero, while the area of the Rh vacancy remained very close to its original value. We note that the measured Rh area exhibits a minor, systematic error, which is presumably due to the nonlinear behavior of the STM piezo element. The modest variation in the Rh vacancy island area (black line) closely resembles the variation in measured position of the island along the horizontal axis (fast scan direction) of Fig. 12.2, including two abrupt jumps that we made to correct for the drift, one at 25 s and the other at 300 s. In order to provide an upper estimate for the number of Rh adatoms (nails) under the graphene, we fit the observed Rh vacancy island areas with the following expression.

$$A_V(t) = [\overline{A_V} - (A_{G0} - A_G(t)) \times P] \times [1 + (D(t) - \overline{D}) \times L] \quad \text{Eq. 12.1}$$

$A_V(t)$ is the expected area of the Rh vacancy island at time t ; $\overline{A_V}$ is the average area of the vacancy before O₂ exposure; A_{G0} is the initial area of the graphene patch; $A_G(t)$ is the remaining area of graphene at time t ; P is the fraction of graphene area that is supported by extra Rh atoms (nails). The second factor between square brackets corrects for the nonlinear piezo effect. Here, $D(t)$ is the distance between the center of the Rh vacancy island and the middle of the (horizontal) scan range at time t . \overline{D} is the average position of the vacancy island, prior to O₂ deposition; L indicates the strength of the image distortion, which we assumed to vary linearly with position within the image. The best-fit value for L was $8.3 \times 10^{-4} \text{ nm}^{-1}$. Calculations for three values of P , namely 0%, 5%, and 10%, are shown in Fig. 12.3B. It is very clear that the best fit is obtained for 0% Rh, i.e. complete *absence* of nails under the graphene, even though 5% Rh would still fall within the measurement accuracy. Note, that 5% would correspond to a nail size of only 6 Rh atoms, which we cannot imagine to be energetically favorable. We therefore conclude that when graphene is formed on Rh(111) the substrate remains flat and does not develop a supporting 'nail' structure.

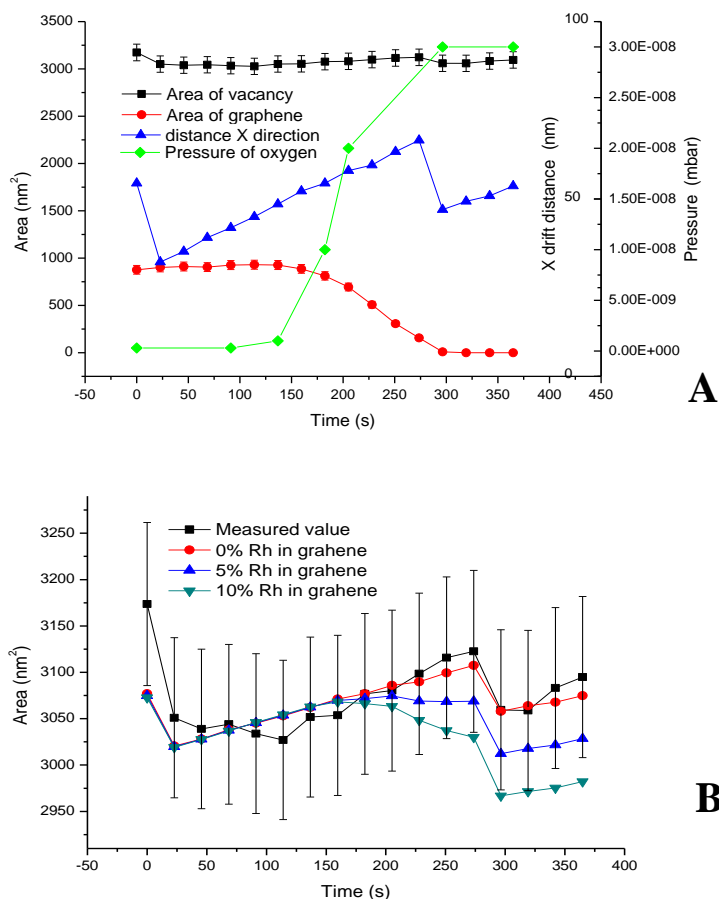


Fig. 12.3 (A) The measured areas of the Rh vacancy island (black) and the graphene patch (red) of Fig. 12.2 as a function of time. The graphene area reduced to zero when O₂ was admitted to the chamber, while the area of the Rh vacancy island did not change significantly. As explained in the text, the residual variation of the Rh vacancy is attributed to the combination of a nonlinearity of the STM scan piezo element and the drifting of the imaged vacancy island along the fast (horizontal) scan direction (blue). The green line is the pressure in the vacuum chamber, not corrected for the specific sensitivity of the pressure gauge to O₂. (B) Fits of the measured area of the Rh vacancy island, obtained with Eq.12.1 for three different values of the assumed coverage of Rh ‘nail’ atoms. The fits take the effect into account of the piezo nonlinearity. The best fit is obtained for 0% Rh, i.e. for the complete absence of nails below graphene on Rh(111).

