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Graphene/Rh(111) Structure Studied Using In-Situ Scanning Tunneling Microscopy *

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Scanning tunnel microscopy (STM) is performed to verify if an Rh 'nails' structure is formed accompanying the graphene growing during chemical vapor deposition. A structure of a graphene island in an Rh vacancy island is used as the start. While the graphene island is removed by oxygenation, the variations of the Rh vacancy island are imaged with an in-situ high-temperature STM. By fitting with our model and calculations, we conclude that the best fit is obtained for 0% Rh, i.e., for the complete absence of nails below graphene on Rh(111). That is, when graphene is formed on Rh(111), the substrate remains flat and does not develop a supporting nail structure.

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Graphene, single-layer graphite, has drawn great attention recently due to its special properties and potential applications, for example, in next-generation electronics.[1,2] However, reproducibly manufacturing high-quality graphene has remained a challenge. The common methods for producing graphene are chemical vapor deposition (CVD),[3–7] liquid-phase exfoliation,[8,9] SiC pyrolysis[10,11] and Hummers' method.[12] To date, most high-quality graphene, for example, used in experiments requiring high carrier mobility, is still obtained from graphite, for example, by the 'scotch-tape' method.[13] Most methods to assemble graphene directly result in materials with high defect densities, caused by multilayer growth,[14–16] and chemical contamination.[17] These imperfections significantly influence the properties and the stability of graphene.

CVD of hydrocarbon molecules on transition metals (TMs) provides a practical method for graphene production. Since newly arriving hydrocarbon molecules do not stick to or decompose on graphene, CVD may lead to precise formation of a single graphene layer, when dissolution and segregation of carbon can be ignored. However, one can also explore the temperature-dependent solubility of carbon in TMs to produce graphene from segregated carbon.[4,18,19] The graphene formation process typically takes place at high temperatures, at which the interaction between carbon and TMs is very complex.[20,21] An essential part of the process, such as the carbon segregation, may take place while the metal substrate is cooled down. Often the properties of graphene are measured only at room temperature or below. From such 'after-growth' observations it is very difficult to distinguish which source of carbon, segregated or directly deposited, has been responsible for the formation of the graphene layer, and what the precise nucleation and growth mechanisms have been. This is why only a limited number of experiments have been devoted to the kinetic processes of this system.[4,5] In addition, most of the experimental methods that can be used *in-situ*, i.e., under growth conditions at high temperature, do not have atomic resolution. Obviously, atomic-scale measurements during graphene growth are really necessary, as they are essential for understanding the nucleation and growth mechanisms, which in turn form the basis for strategies for improving the quality of grown graphene. In the previous research, we have utilized an *in-situ* high-temperature scanning tunnel microscopy (STM) to study the growing process of graphene on several TMs, and addressed the influence of not only the conventional growth parameters, in this case the temperature and the ethylene pressure, but also the starting situation.[22] Armed with this information, we propose a first recipe for growing high-quality graphene and conclude that the final quality of the graphene overlayer is limited by the formation of a special double-layer Rh island structures. Based on the appearance of these structures, we provide a detailed, quantitative analysis of various aspects of the growth kinetics. In this study, we use the same *in-situ* observation method to determine a structure controversy of graphene on TMs.

It has been proposed that graphene is supported by an Ru nail structure on Ru(0001), with one nail under each unit cell of the moiré pattern, as shown in Fig. 1.[23] The nails have a height of one atomic layer

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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 nano-patterns, e.g., regular arrays of metal nanoparticles.

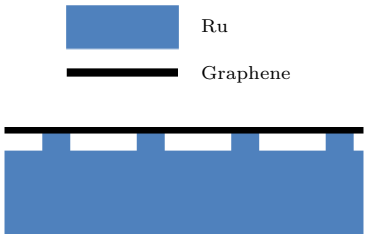

Fig. 1. Sketch of the 'nails' under the graphene layer on Ru(0001). Ru forms monolayer high nails on the Ru surface that support the graphene structure and reduce unfavorable interaction between the graphene and the Ru substrate.[23]

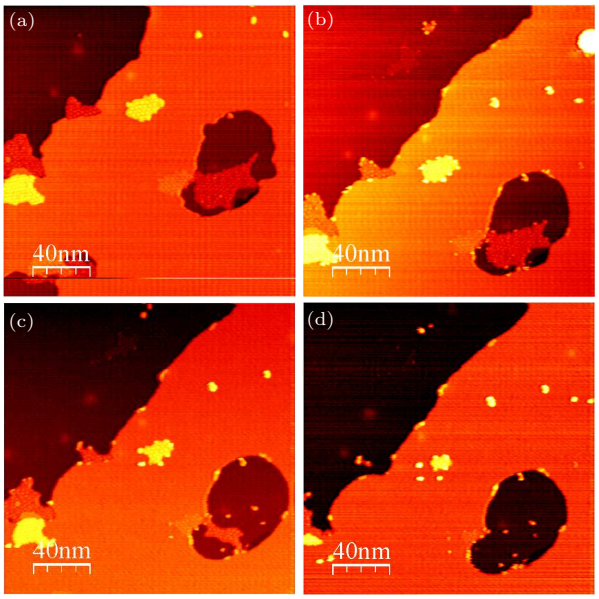

Fig. 2. Four snapshots from an STM measurement, in which an Rh vacancy island with a graphene patch inside is exposed to O_2 at 745 K. (a) The initial situation of this structure. (b) Here 60 s after the start of the exposure part of the graphene island is reacted away. (c) After 251 s, most of the graphene island is removed. (d) Complete removal of the graphene patch is obtained after 319 s. The sizes of all images are $200\times200\,\mathrm{nm}^2$, which have been taken at a sample voltage of $V_\mathrm{b} = -0.75$ V and a tunneling current of $I_\mathrm{t} = 0.05$ nA. The frame rate is 22.8 s/frame.

Since Rh(111) and Rh(0001) are very similar for graphene growth,[24] we also consider that a similar structure can be present on Rh(111). Our *in-situ* growth movies of graphene on Rh(111) in the study published previously[25] 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 has formed. 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 graphene.

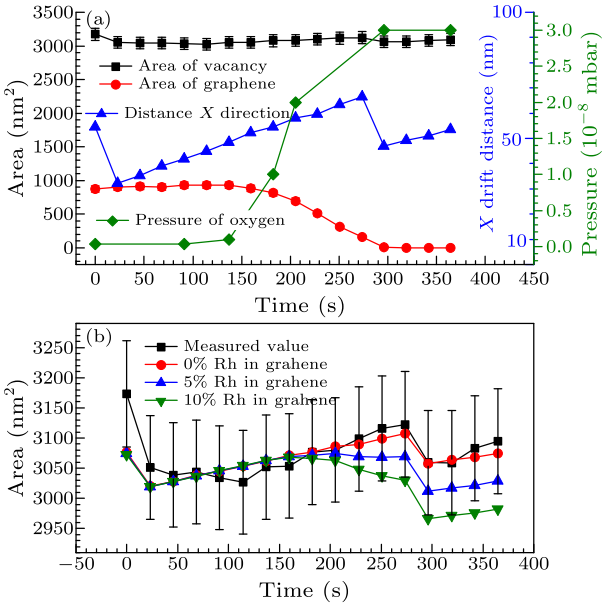

Fig. 3. (a) The measured areas of the Rh vacancy island (black) and the graphene patch (red) in Fig. 2 as a function of the time. The graphene area reduces to zero when O_2 is admitted to the chamber, while the area of the Rh vacancy island does not change significantly. As is explained, the residual 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 O_2. (b) Fits of the measured area of the Rh vacancy island, obtained with Eq. (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).

All measurements were performed under ultrahigh vacuum (UHV) environment with an STM, which can be applied under actual process conditions, i.e., at elevated temperatures and during substantial variations in temperature. Temperatures were measured by a K-type thermocouple, spot-welded onto the sample. Gas pressures were measured by an ionization gauge (Instrutech®, Inc., CVG101). A clean Rh(111) surface[26] was chosen to expose in ethylene. The geometry that we designed for this experiment is that of a vacancy island on Rh(111), partly covered by graphene. To create such a geometry, we first bombarded the clean Rh(111) surface by 400 eV Ar^+ ions for 10 min at room temperature, and slowly warmed up the sample to 800 K. STM measurement was performed to monitor the size and density of the vacan-

cies 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 too small to 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 of ethylene gas. Again the sample was slowly annealed, this time to 870 K, 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. Figure 2(a) shows the typical geometry obtained by this preparation procedure.

To explore the possible presence of Rh atoms that were supporting the graphene in the Rh vacancy islands, we exposed the surface to O_2 at 745 K, thereby removing the graphene layer (Figs. 2(b)–2(d)). We assume that it is very difficult for Rh adatoms to diffuse out of a vacancy island in the Rh substrate. Thus 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 which were originally in the nails would join the inner edge of the Rh vacancy island.

Figure 3 shows the measured areas of the Rh vacancy island and the graphene patch in Fig. 2 as a function of the time (several islands was measured and similar results were obtained). Several STM images were measured before and after the oxygenation process, to test for systematic errors, for example, ripening of the Rh island. After O_2 had been admitted into the chamber (the increase of the green line in Fig. 3(a)), 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. 2, including two abrupt jumps that we made to correct for the drift, one at 25 s and the other at 300 s. To provide an upper estimate for the number of Rh adatoms (nails) under the graphene, we fit the observed Rh vacancy island areas with

$$A_{\mathrm{V}}(t) = [\bar{A_{\mathrm{V}}} - (A_{\mathrm{G0}} - A_{\mathrm{G}}(t)) \times P] \times [1 + (D(t) - \bar{D}) \times L], \quad (1)$$

where $A_{\mathrm{V}}(t)$ is the expected area of the Rh vacancy island at time t, $\bar{A_{\mathrm{V}}}$ is the average area of the vacancy before O_2 exposure, $A_{\mathrm{G0}}A_{\mathrm{G0}}$ is the initial area of the graphene patch, $A_{\mathrm{G}}(t)$ is the remaining area of graphene at time t, and 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, $\bar{D}$ is the average position of the vacancy island, prior to O_2 deposition, and L indicates the strength of the image distortion, which is assumed to vary linearly with position within the image. The best-fit value for L was $8.3 \times 10^{-4}\,\mathrm{nm}^{-1}$. Calculations for three values of P: 0%, 5%, and 10%, are shown in Fig. 3(b). 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 obtain that when graphene is formed on Rh(111), the substrate remains flat and does not develop a supporting nail structure.

In summary, we have studied the formation of graphene on Rh (111) during the CVD. By measuring the Rh vacancy island before and after the oxygenation process, we obtain that when graphene is formed on Rh(111), the substrate remains flat and does not develop a supporting nail structure. This result can be adapted easily to graphene formation on other TMs and is therefore useful in interpreting this class of growth systems in general and in optimizing growth recipes for each of these cases.

References

[1] Castro-Neto A H et al 2009 *Rev. Mod. Phys.* **81** 109
[2] Britnell L et al 2012 *Science* **335** 947
[3] Oshima C et al 2000 *Surf. Rev. Lett.* **7** 521
[4] Loginova E, Bartelt N C, Feibelman P J and McCarty K F 2009 *New J. Phys.* **11** 063046
[5] McCarty K F, Feibelman P J, Loginova E and Bartelt N C 2009 *Carbon* **47** 1806
[6] Wintterlin J and Bocquet M L 2009 *Surf. Sci.* **603** 1841
[7] Artyukhov V I, Liu Y Y and Yakobson B I 2012 *Proc. Natl. Acad. Sci. USA* **109** 15136
[8] Lotya M et al 2009 *J. Am. Chem. Soc.* **131** 3611
[9] Englert J M et al 2011 *Nat. Chem.* **3** 279
[10] Zhou P and He D W 2016 *Chin. Phys.* B **25** 017302
[11] Deng P F et al 2013 *Chin. Phys. Lett.* **30** 018101
[12] Hummers S and Offeman R 1958 *J. Am. Chem. Soc.* **80** 1339
[13] Novoselov K S et al 2004 *Science* **306** 666
[14] Kim K S et al 2009 *Nature* **457** 706
[15] Reina A et al 2009 *Nano Lett.* **9** 30
[16] Bi H et al 2012 *Carbon* **50** 2703
[17] Guo H L et al 2009 *ACS Nano* **3** 2653
[18] Sett L C and Blakely J M 1976 *Surf. Sci.* **58** 397
[19] Yu Q K et al 2008 *Appl. Phys. Lett.* **93** 113103
[20] Gao T et al 2015 *Nat. Commun.* **6** 6835
[21] Wang J, Zhao R, Liu Z and Liu Z 2013 *Small* **9** 1373
[22] Dong G C and Frenken J W M 2013 *ACS Nano* **7** 7028
[23] Starodub E et al 2009 *Phys. Rev.* B **80** 235422
[24] Gao J F and Ding F 2014 *Angew. Chem. Int. Ed.* **53** 14031
[25] Dong G C, van Baarle D W, Rost M J and Frenken J W M 2012 *New J. Phys.* **14** 053033
[26] Delouise L A and Winograd N 1984 *Surf. Sci.* **138** 417