Effects of graphene defects on Co cluster nucleation and intercalation*

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Four kinds of defects are observed in graphene grown on Ru (0001) surfaces. After cobalt deposition at room temperature, the cobalt nanoclusters are preferentially located at the defect position. By annealing at 530 °C, cobalt atoms intercalate at the interface of Graphene/Ru (0001) through the defects. Further deposition and annealing increase the sizes of intercalated Co islands. This provides a method of controlling the arrangement of cobalt nanoclusters and also the density and the sizes of intercalated cobalt islands, which would find potential applications in catalysis industries, magnetism storage, and magnetism control in future information technology.

Keywords: graphene, defects, cobalt, intercalation, scanning tunneling microscopy

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1. Introduction

Graphene, a single layer of carbon atoms densely packed by sp^2 hybrid bonding, is a potential candidate for many applications due to its outstanding structural, electronic, mechanical, and thermal properties.[1–3] One of these applications is for it to be used as a thin film template to control the size and arrangement of metal nanoclusters.[4] Metal nanoclusters exhibit the quantum size effect[5] and unusual chemical reactivity,[6] which could be utilized widely in electronics and catalysis industries. In particular, cobalt nanoclusters exhibit strong magnetism.[7] The arrangement of Co clusters on a graphene template may be affected by the structural defects in graphene. Therefore, using graphene with defects as a template to control the size and arrangement of metal nanoclusters can produce new phenomena and offer a broad potential for useful applications.

2. Methods

Our experiments were carried out in a UHV system with a base pressure lower than 2×10^{-10} mbar (1 bar = 10^5 Pa). The system is equipped with an Omicron room temperature scanning tunneling microscope (RT-STM), an electron beam heater (EBH), a low energy electron diffraction (LEED), a UHV evaporator with a cobalt rod (purity of 99.995%, Alfa Aesar), and a gas station that can introduce ethylene (purity of 99.995%, Beijing Huayuan Gas Chemical Industry Co., Ltd) into the UHV chamber through a leak valve. Epitaxial growth of graphene on metals[8–11] is a very important method to produce graphene. Single-crystal Ru (0001), purchased from MaTeck, was used as the substrate for the epitaxial growth of graphene. The Ru (0001) surfaces were prepared by repeated cycles of Ar^+ sputtering and annealing in oxygen at 800 °C to remove the residual carbon, and then flashing to 1300 °C to remove the oxide.[12] The surface order and cleanliness were verified by LEED, Auger electron spectroscopy (AES), and STM. The graphene layer was prepared by thermal decomposition of ethylene on a Ru (0001) surface at a temperature of 800 °C.[12]

3. Results and discussion

It is well known that the graphene grown on Ru (0001) substrate forms a regular Moiré pattern; there are three different sites, i.e., atop, fcc, and hcp sites within the Moiré unit cell.[13] In our experiments, two kinds of point defect are found, i.e., adatoms and vacancies. As shown in Fig. 1(a), an contaminant adatom is located in the hcp region of the graphene/Ru (0001) Moiré structure. No interference is observed around this adatom defect in the atomic-resolved STM images, which concludes the intactness of the graphene structure. The other kind of point defect, i.e., vacancy, is shown in Fig. 1(b). Unlike the adatom, the loss of carbon atoms in the graphene structure leads to a complex interference around the defect position, which is different from the interference patterns in free-standing graphene, owing to strong interactions between the graphene and the Ru substrate.[14] Besides

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point defects, two kinds of line defects are shown in Figs. 1(c) and 1(d). The most common line defects are graphene edges as shown in Fig. 1(c). In the upper-left and middle parts of the image, the graphene/Ru (0001) structure with Moiré pattern is shown, while other parts of the surface are covered by amorphous carbon. The surface step edge of the Ru crystal is another important source of the line defects. In most cases a graphene sheet grows in the 'downhill' direction and can flow uninhibitedly in a carpet-like fashion across the step.[15] However, we also find that steps might interrupt the expansion of graphene and induce line defects along step edges as shown in Fig. 1(d). One possible reason could be that there are two nucleation centers on the two terraces of the Ru (0001) surface from which two graphene sheets develop separately. In total, four kinds of defect are found, i.e., two point defects and two line defects.

After the growth of graphene on Ru surfaces, cobalt atoms are deposited from the cobalt evaporator onto the graphene Moiré template at room temperature. An STM image of graphene after cobalt deposition is shown in Fig. 2(a). The cobalt forms three-dimensional (3D) clusters whose bottom diameter and height are typically ~ 5 nm and ~ 2 nm respectively; each cluster contains hundreds of cobalt atoms (Figs. 2(b) and 2(c)), which is different from the monodispersed Pt nanocluster with a preferred nucleation region on the Moiré template of graphene/Ru (0001).[4] On defect-free graphene surfaces, cobalt clusters nucleate randomly on the surface at the coverage of 0.02 ML (Fig. 2(a)), while on the graphene with defects, cobalt cluster nucleation possesses different properties. A series of STM images with Co coverages of 0.02, 0.06, and 0.36 ML is shown in Figs. 2(d)–2(f). A large proportion of cobalt clusters are located near defects in graphene as shown in Fig. 2(d). We infer that the cobalt atom preferential adsorptions in these regions are due to the bigger adsorption energies at these positions which come from dangling bonds of the carbon atoms or bare ruthenium surface at defects. At increasing coverages, a large proportion of cobalt clusters nucleate near point defects in graphene while few cobalt clusters are located at the line defects on steps as shown in Fig. 2(f). Therefore, defects in graphene whose density can be controlled by the sputtering of ions/electrons or growth conditions provide a method to modulate the arrangement of cobalt nanoclusters on graphene.

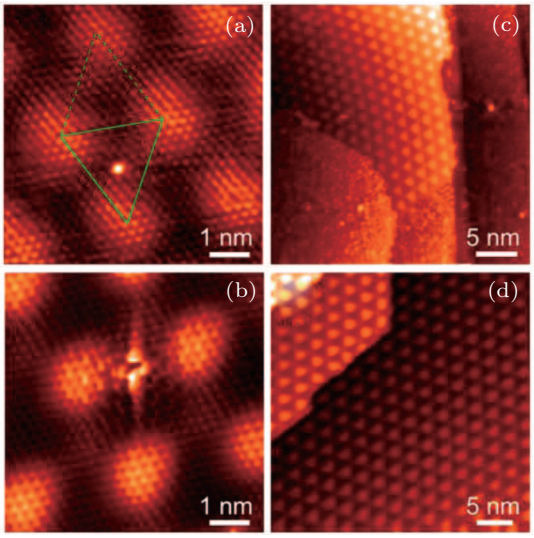


Fig. 1. (color online) STM images of different kinds of defects in graphene. (a) STM image of graphene with adatom. The Moiré unit cell is shown, in which the atop sites are the bright area, and hcp and fcc sites are marked by the solid and dotted lines, respectively. (b) STM image of graphene with vacancy. (c) STM image of graphene with edges next to the surface covered by amorphous carbon. (d) STM image of graphene with edge on the step edge of Ru substrate.

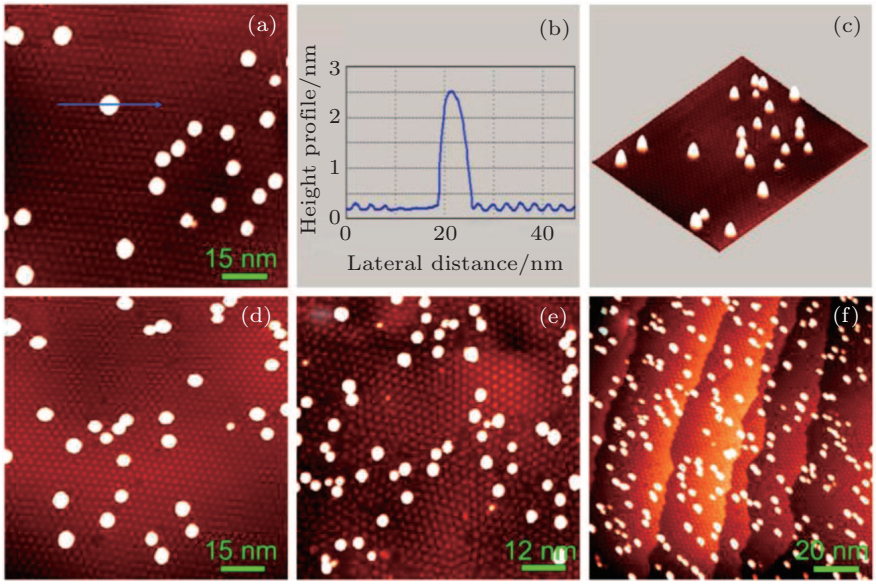


Fig. 2. (color online) STM images of graphene with cobalt clusters. (a) STM image of graphene without defects after cobalt deposition. (b) Line profile along the blue line shown in panel (a). (c) Corresponding 3D image of panel (a). (d)–(f) STM images of graphene with defects after cobalt deposition at 0.02 ML (d), 0.06 ML (e), and 0.36 ML (f).

There is a strong interaction between epitaxial graphene and the Ru substrate, which disturbs many unique electronic properties of graphene. Previous studies have reported that the interaction can be effectively weakened by the intercalation of other elements, such as noble metals Ag,[16,17] Pt,[18] Pd,[18] and Au,[18–21] magnetic metals Ni[18] and Co,[18] the IIIA group metal In,[18] the rare earth metal Ce,[18] and Cu,[22] between epitaxial graphene and the substrate. Here, we report the influence of defects in graphene on cobalt intercalation between epitaxial graphene and the Ru substrate. Cobalt atoms intercalate between graphene and Ru (0001) when annealing at 530 °C. After Co intercalation, graphene exhibits a similar Moiré pattern on the intercalated structures to that on Ru (0001), which is shown by STM images in Fig. 3(a). Most of the intercalated cobalt islands are under or near defects in graphene. It can be inferred that the defects in graphene afford a path for the intercalation process of cobalt atoms. We deposit additional Co atoms onto the Co interacted graphene sample, find that the additional Co atoms form nanoclusters and the arrangement of cobalt nanoclusters is also affected by defects in graphene, as the topographic image demonstrates in Fig. 3(b). After subsequently annealing at 530 °C again, all the cobalt atoms on the graphene intercalate between graphene and Ru (0001), and the sizes of the intercalated cobalt islands increase. But the density of intercalated cobalt islands almost remains the same as that in the first cobalt intercalation cycle, which is because the density of defects in graphene does not change in the process. Accordingly we can control the density and size of intercalated cobalt islands by adjusting the density of the defects and the coverage of the Co atoms. Considering the magnetism of cobalt clusters and the protection from the inert graphene layer, this intercalated graphene/Co/Ru (0001) structure would be very useful in many fields.

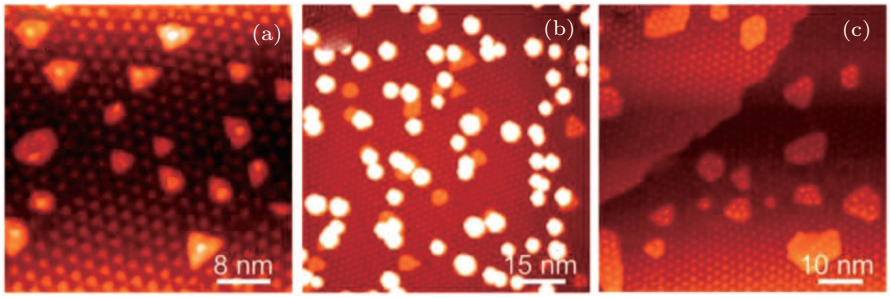


Fig. 3. (color online) STM images of graphene after cobalt intercalation. (a) STM image of graphene after cobalt deposition and annealing at 530 °C. The brighter parts of the image are cobalt islands under graphene. (b) STM image of graphene after cobalt intercalation and the additional cobalt deposition. (c) STM image of graphene after two cycles of cobalt intercalation.

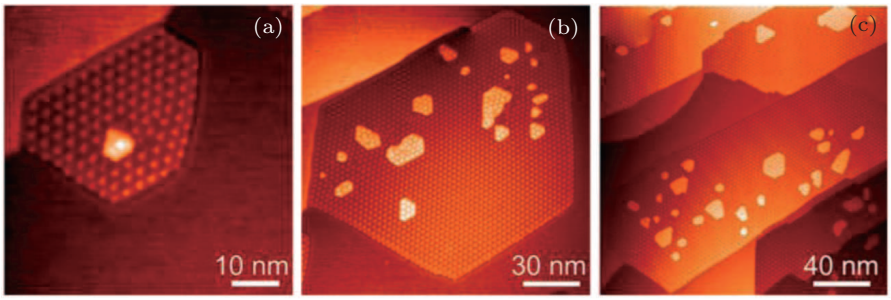


Fig. 4. (color online) STM images of graphene islands with different sizes after cobalt intercalation. (a) STM image of a graphene island with a lateral size of about 40 nm after cobalt intercalation. The brighter part of the graphene island is the cobalt island under the graphene. (b) STM image of a graphene island with a lateral size of about 150 nm after cobalt intercalation. (c) STM image of graphene islands with lateral sizes exceeding 250 nm after cobalt intercalation.

In addition to one full monolayer continuous graphene, cobalt intercalation on graphene islands is also explored. The method of growing graphene islands is temperature-programmed growth (TPG). The Ru (0001) substrate is exposed to 100-L ethylene at room temperature, followed by annealing at 830 °C. The sample is kept at that temperature for 30 s and then cooled down to room temperature at a rate of 0.5 °C·s^{-1}.[23] STM topographic images (Figs. 4(a)–4(c)) show the graphene islands after cobalt intercalation. Like the case of cobalt islands under full monolayer graphene, the intercalated cobalt islands also mostly located under or on the neighborhood of defects in the graphene islands. For different sizes of graphene islands there are only a few intercalated cobalt islands near the edge of graphene islands, which may be

attributed to the fact that most of cobalt atoms near the edge of graphene islands diffuse into bare Ru surface during annealing. These observations further demonstrate that the defects in graphene benefit the formation of a cobalt intercalated structure under graphene.

4. Conclusions

We present four kinds of defects in graphene on Ru (0001). The deposited cobalt atoms prefer to be located near these defects and demonstrate a distribution of nanoclusters on graphene at room temperature. The arrangement and density of cobalt nanoclusters on graphene are modulated by controlling the density of defects in graphene. After the sample is annealed, cobalt atoms intercalate under graphene and form intercalated cobalt islands neighboring the defects. The additional deposition and intercalation cycles increase the sizes of intercalated cobalt islands without changing the density of cobalt islands. Therefore our work affords a method to modulate the density of cobalt nanoclusters and the arrangement of intercalated cobalt islands under graphene by artificially controlling the density of defects in graphene. This would be very useful in catalysis industries, magnetism storage, and magnetism control in future information technology.

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