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Formation of graphene on Ru(0001) surface*

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We report on the formation of a graphene monolayer on a Ru(0001) surface by annealing the Ru(0001) crystal. The samples are characterized by scanning tunnelling microscopy (STM) and Auger electron spectroscopy (AES). STM images show that the Moiré pattern is caused by the graphene layer mismatched with the underlying Ru(0001) surface and has an $N \times N$ superlattice. It is further found that the graphene monolayer on a Ru(0001) surface is very stable at high temperatures. Our results provide a simple and convenient method to produce a graphene monolayer on the Ru(0001) surface, which is used as a template for fabricating functional nanostructures needed in future nano devices and catalysis.

Keywords: graphene, Ru (0001), Moiré pattern, STM
PACC: 8120V, 0779, 6820

Graphene has aroused a great interest because of its novel properties[1−3] and potential applications.[4−8] All the existing methods that have been utilized up to now are the micromechanical cleavage or chemical exfoliation of highly oriented pyrolytic graphite (HOPG),[9−12] thermal decomposition of SiC,[13−15] epitaxial growth by a vapour phase deposition of hydrocarbons or CO on metal substrates.[16−18] However, the problem of efficiently synthesizing the single- and few-layer graphene still exists, i.e. low efficiency and poor crystallinity. The graphene prepared by cleavage of HOPG has a very high quality of crystallinity as predefined in HOPG, but the productivity is very low and the size of the crystalline graphene is on the order of only about a few microns. Graphene layers formed on a SiC surface usually contain multiple domains, poor long-range order, and structural defects.[15] Vapour phase growth on metal substrates very often leads the graphene to form only on a portion of the substrate surface.[19] In order to realize practical application of the graphene, new method of producing graphene is needed. In this paper, we report on the formation of a large-scale graphene layer with a high quality on a Ru (0001) surface by segregating the carbon impurity from the bulk.

The experiment was carried out in an ultra-high vacuum (UHV) chamber at a base pressure lower than 1×10^{-8} Pa. The chamber was equipped with a room temperature scanning tunnelling microscope (STM), an Auger electron spectrometer (AES), and an electron beam heating (EBH) stage. The Ru single crystal wafer, with a diameter of 8 mm and a thickness of 1 mm was a commercial product whose (0001) surface had been polished to a roughness less than 0.03 μm. It was cleaned by 3 cycles of ultrasonic cleaning in high-purity acetone and ethanol to remove the organic contamination from the surface. Then the Ru crystal wafer was loaded into the UHV chamber and pretreated by using cycles of 0.8 keV Ar^+ sputtering then annealed at up to 1350 K until clean AES peaks of Ru without notable impurity peaks were observed. The temperature was measured by a tungsten–rhenium (W–5%Re/W–26%Re) thermocouple welded to the EBH stage. The wafer was annealed in the following steps: slowly raising the temperature at a pressure no higher than 1×10^{-7} Pa, staying at 1000 K for 20 min and slowly cooling down to room temperature. Afterwards, a graphene layer grew on the Ru surface, which was characterized in situ by STM, and AES. The AES spectra were obtained at an electron beam energy of 3 kV.

The STM images of the annealed substrate surface are shown in Fig.1. In Fig.1(a) there can be found a wide atomic flat terrace and several steps on the top right corner. The wide terrace is fully covered by many hexagonally arranged protrusions. Figure 1(c) is a height profile of the arrowed steps in Fig.1(a). This profile indicates that the average distance between the neighbouring protrusions is 3 nm and their

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average height is 0.1 nm. On the neighbouring terraces, the protrusion arrays keep the same orientations. Figure 1(b) is an atomic resolution STM image of a small area on the terrace. It can be seen that the protrusions have hexagonal structure of small spots. Figure 1(d) shows the height profile along the arrow direction in Fig.1(b). The average distance between spots is 0.25 nm, which agrees very well with the lattice constant of graphene.

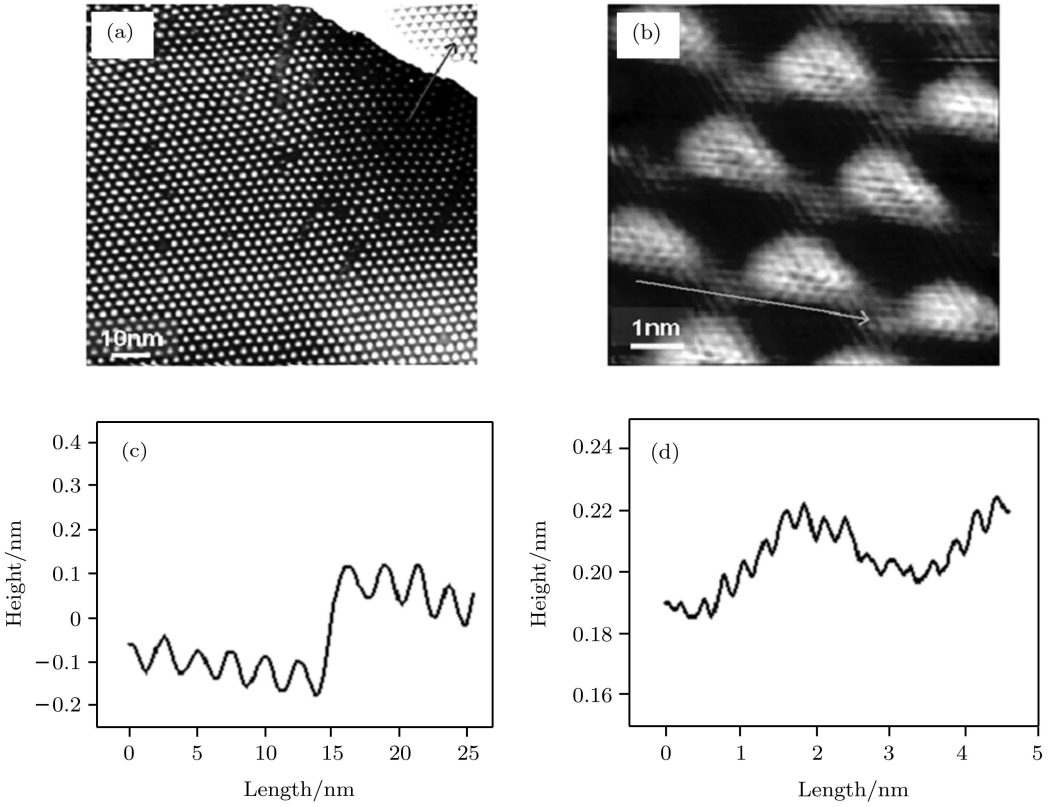
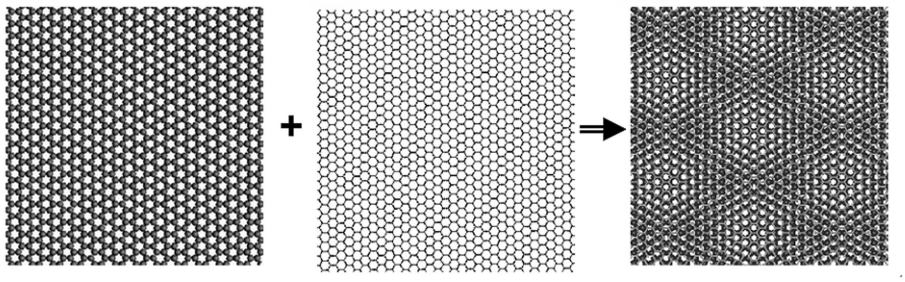


Fig.1. (a) An STM image of graphene overlayer on Ru (0001) surface after annealing at 1000 K with tunnelling parameters being $V_s = 0.3$ V and $I = 0.11$ nA. The protrusions show Moiré pattern. (b) An atomic resolution STM image of the graphene overlayer with tunnelling parameters being $V_s = 0.03$ V and $I = 0.4$ nA. (c) Height profile along the arrowed step in (a). (d) Height profile along the arrow direction in (b).

The protrusions in Fig.1(a) show the Moiré pattern, which were explained to result from the superimposition of two structures with different lattice constants and/or orientations in Ref.[20]. However, the Moiré pattern in this experiment originates from the superimposition of graphene overlayers on the Ru (0001) surface, as shown in Fig.2. Figures 2(a) and 2(b) show the lattice structures of the Ru (0001) surface and the single-layer graphene flake respectively. When the two images are superimposed together, they form a superstructure as shown in Fig.2(c). Because the lattice constant of graphene is different from that of Ru, each carbon atom is located at different site of the substrate in a unit cell of the superstructure. These carbon atoms appear as spots with different brightnesses in atomic resolution STM image (see Fig.1(b)). As a result, on a large scale the superstructure appears as protrusions and hollows, which are similar to those in the image shown in Fig.1(a) and 1(b).

We also conducted the AES analyses of the samples before and after annealing them to confirm the element compositions in the new structure. As shown in Fig.3, the curve with open circles shows the AES spectrum before annealing. There are four peaks located at 273, 230, 200, and 150 eV, respectively, which are attributed to Ruthenium MNN Auger electrons.[21] The curve with solid circles show the AES spectrum after annealing. In this curve, the intensities of the peaks at 230, 200, and 150 eV, remain the same as the previous ones. However, the intensity of the peak at 273 eV becomes higher. This is because of the contri-



(a) (b) (c)

Fig.2. Schematic model for the formation of Moiré pattern of graphene overlayer on Ru (0001) surface. (a) Lattice structure of the cleaved Ru (0001) surface. (b) Lattice structure of the single-layer graphene. (c) Superimposition of (a) and (b), forming the hexagonal superstructure of the Moiré pattern.

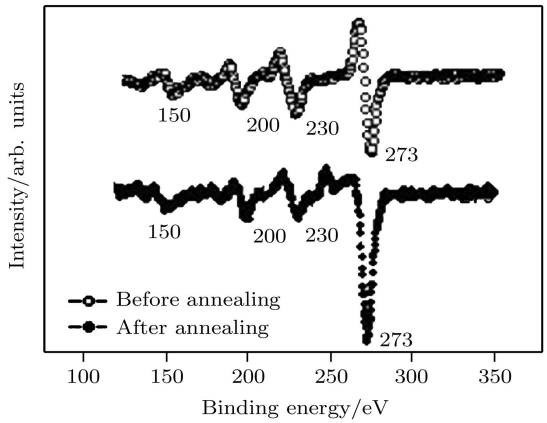


Fig.3. AES spectra before (the curve with open circles) and after (the curve with solid circles) annealing, indicating the carbon present in the overlayer.

bution of carbon KLL Auger electron at 272 eV.[22] These AES spectra demonstrate that the new structure contains carbon indeed, which segregated from the bulk and accumulated on the surface during the annealing.

In conclusion, we have prepared a graphene monolayer on a Ru (0001) substrate by thermal annealing. The chemical composition in the overlayer is demonstrated with AES to be of carbon. The Moiré pattern analysis indicates that the formed overlayer on Ru (0001) surface is of graphene. This new method of producing graphene has a very high productivity, which may open the way to a practical application of graphene to future electronic devices and catalysis.

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