Silicon intercalation at the interface of graphene and Ir(111)

Lei Meng, Rongting Wu, Haitao Zhou, Geng Li, Yi Zhang, Linfei Li, Yeliang Wang,a) and H.-J. Gaoa)

Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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We report on the structural and electronic properties in the heterostructure of graphene/silicon/Ir(111). A $(\sqrt{19} \times \sqrt{19})$R23.41° superstructure is confirmed by low energy electron diffraction and scanning tunneling microscopy and its formation is ascribed to silicon intercalation at the interface between the graphene and the Ir(111) substrate. The dI/dV measurements indicate that the interaction between graphene and Ir is effectively decoupled after silicon intercalation. Raman spectroscopy also reveals the vibrational states of graphene, G peak and 2D peak, which further demonstrates that the silicon-buffered graphene behaves more like intrinsic graphene. © 2012 American Institute of Physics. [doi:10.1063/1.3687688]

Since graphene (Gr)—a single layer of sp² bonded carbon lattice—was exfoliated from graphite in 2004,1 researchers have demonstrated various unique properties—electronic, magnetic, and optical2–5—which in turn have aroused considerable interest in scientific and technological fields, with particular attention to preparing high quality industrial-scale graphene sheets. One established method is epitaxial growth on transition metal substrates,6–11 which favor the formation of graphene by serving as both catalyst and template. Nevertheless, in these Gr/metal systems, some interaction generally exists between graphene and its metal host, which affects the intrinsic electronic structure of graphene to some degree. For example, high quality graphene can be prepared on Ir(111) substrate,8 but its π band is hybridized by the Ir 5d state. (The lattice of such graphene is aligned with that of the substrate.) This hybridization makes the vibrational states of graphene invisible in the Raman spectra.12

In order to overcome the effect of a transition metal substrate on the intrinsic electronic structure of epitaxial graphene, a buffer layer can be built to weaken the interaction. For example, intercalated layers of metal elements13–17 or molecules18 are reported. Very recently, silicon, a semiconductor element, was introduced as the interfacial layer between graphene and its metallic host in the system of Gr/Ru(0001), which effectively weakens the interaction between graphene and ruthenium.19 In this regard, silicon buffer layers play a particularly important role, since this semiconductor material makes it possible to directly insert an insulating interface between graphene and underlying metal. Such a graphene/insulator/metal heterostructure could be compatible with current microelectronic technology and provide the advantages of device integration based on large-scale graphene. Comparing the interactions within the Gr/Ru(0001) system to those in Gr/Ir(111), the latter is reported to be much weaker, based on x-ray photoemission spectroscopy (XPS) measurements,20 so it provides a chance to test the possibility of silicon interaction at different Gr/metal interfaces and to evaluate the effect of silicon layers on the electronic properties of graphene. Recent findings stimulated us to intercalate a silicon layer between graphene and Ir(111). In the present work, we fabricate such structures and characterize the geometric and electronic properties at the buffered interface.

Graphene was fabricated by chemical decomposition of ethylene on an Ir(111) surface. Then, we deposited silicon on the Gr/Ir(111) sample and annealed it at 800 K, whereupon a distinct superstructure emerged and was characterized by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). We also confirmed that the appearance of this superstructure is due to the silicon intercalation. We further investigated the electronic properties of the system using dI/dV measurements and Raman spectroscopy on both Gr/Ir and Gr/Si/Ir, confirming that the silicon intercalation does decouple the interaction between graphene and the Ir substrate.

More specifically, our experiment was performed in an ultra-high vacuum (UHV) system with a base pressure about $2 \times 10^{-10}$ mbar. The Ir(111) substrate was cleaned by several cycles of sputtering and annealing till it yielded a distinct Ir $(1 \times 1)$ diffraction spot in an LEED pattern and a clean surface in STM images. Graphene was fabricated by exposing ethylene for 80 s to the Ir substrate kept at 1120 K, followed by an annealing treatment at 1570 K. The silicon was deposited at room temperature from a piece of silicon heated by a direct current about 4 A for 1 h. After deposition, the sample was annealed at 800 K for 30 min in UHV condition. To characterize its properties, we employed STM for imaging the surface and doing dI/dV spectroscopy at a low temperature of 5 K. Raman spectra were acquired by a Renishaw spectrometer at 532 nm with 1 mW power.

The quality of graphene was first identified by the LEED pattern macroscopically. In Fig. 1(a), the inner six spots and the outer six spots, indicated by the dashed-line and solid-line arrows, can be easily distinguished and assigned to the Ir(111) lattice and the graphene adlayer, respectively. The additional satellite spots can be ascribed to the moiré superstructure of graphene and are caused by the mismatch between graphene and the Ir substrate. Such a LEED pattern confirms that epitaxially grown graphene has been formed on the Ir(111) surface. Moreover, besides the six spots from graphene, no other rotational spots are found...

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a)Electronic addresses: ylwang@iphy.ac.cn and hjgao@iphy.ac.cn.
and 67 eV, respectively. Instead, some distinct superstructure emerged, which was confirmed by the LEED adlayer (not shown here). After annealing at 800 K, a new clusters showed a dispersed distribution on the graphene adlayer, and that graphene that region A is denoted by a solid line; region B has another orientation which is denoted by a dashed line. The angle between these two orientations is about 13.2°. Based on the above analysis of the LEED pattern and STM images, this silicon-induced superstructure can be determined as a (√19 × √19) moiré superstructure. This superstructure holds two symmetrical orientations, which are consistent with that of two observed regions here. In addition, regions like A are located at step edges and regions like B are located within the graphene adlayer. These locations with a random distribution indicate that the intercalation occurs both at the terrace and the step edges, suggesting that silicon intercalation starts both at the step edges and on the terraces.

Next, we further expound the arrangement of the graphene adlayer and the intercalated Si layer. Figure 2(a) shows the domain boundary, denoted by the black dashed line, between a Gr/Ir area (with a periodicity of 2.5 nm) in the lower-right and a silicon-intercalated Gr/Si/Ir area (periodicity 1.2 nm) in the upper-left. It is easy to see several key features in the intercalated area: graphene honeycomb lattice, (√19 × √19)R23.41° superstructure and even the silicon lattice underneath the graphene. The corresponding fast Fourier transform (FFT) pattern (Fig. 2(b)) reveals the information more clearly. The pattern can be described as four distinct circles of spots, each including six spots with hexagonal symmetry. In more detail, the innermost circle is associated with the 2.5 nm moiré pattern caused by the mismatch between graphene and the Ir(111) lattice; the second circle arises from the (√19 × √19)R23.41° moiré superlattice induced by silicon intercalation; the third, larger one indicates a superstructure with a much smaller periodicity of about 0.44 nm which we suppose to be the periodicity of the silicon structure formed underneath the graphene; and the outermost circle of spots is obviously from the lattice of graphene, which has the smallest periodicity, 0.25 nm.

In Fig. 2(a), some dark sites (highlighted by the solid rectangles) are visible in the area of Gr/Si/Ir. There are three plausible explanations for these dark sites. First, the carbon atoms are missing from these sites. Second, the atoms in the dark area are lower than other atoms in the surface geometry. Third, the local density of states (LDOS) at the dark site is less dense than at other sites. Upon removing the third large circle of spots (0.44 nm in periodicity) from the FFT pattern by a high-pass treatment (see Fig. 2(d)), we get an image that nicely reveals the honeycomb lattice of the topmost graphene layer, as shown in Fig. 2(c). We see no sign of defects in this topmost lattice, so the first proposed explanation, missing carbon atoms, is ruled out. Since the applied bias voltage (Vs = −0.05 V) of this image is very close to Fermi level, the image would be related to dI/dV mapping. Thus, we think that the darkness of certain sites in the STM image is probably due to the relatively low LDOS at those sites, although it is hard to exclude the effect of geometric

FIG. 1. (Color online) LEED patterns and STM images of graphene on Ir(111) before and after silicon intercalation. (a) Before intercalation, the inner six spots and the outer six spots, indicated by the dashed-line and solid-line arrows, are from Ir(111) and graphene adlayer, respectively. (b) Large-scale image (U = −1.54 V, I = 0.05 nA) shows a well ordered graphene adlayer with a moiré superstructure of 2.5 nm. Inset is a zoomed-in image with atomic resolution, inside a model superimposed on graphene indicating its orientation. (c) After silicon intercalation, a group of new spots appear within the circle of Ir(111) diffraction spots. (d) STM image (U = −0.38 V, I = 0.13 nA) showing two distinct ordered domains (marked as A and B) with a periodicity of 1.2 nm. (a) and (c) are obtained at 70 eV and 67 eV, respectively.
corrugation. Therefore, we conclude that the graphene lattice on Ir substrate after silicon intercalation is still continuous and intact.

Next, we try to understand the ordered silicon layer beneath graphene. As discussed above, the spots in the third large circle of the FFT pattern in Fig. 2(b) indicates an ordered superstructure of silicon with a periodicity of 0.44 nm. In order to get a clearer picture of this silicon structure, we eliminated the information of the topmost graphene layer (2.5 nm lattice) from inner to outmost circles. Omitting the information of the superstructure with a periodicity of 0.44 nm and 0.25 nm, as seen in (d) and (f), the corresponding STM images are shown in (c) and (e). From this, we can see that the topmost graphene layer (2.5 nm lattice) is intact and continuous in (c), and the underlying silicon layer (1.2 nm lattice) has a honeycomb structure in the upper-left region in (e).

To further examine the electronic properties of graphene on Ir substrate with intercalated silicon, dI/dV spectroscopy was performed locally on both Gr/Ir and Gr/Si/Ir areas. The measurements shown in Fig. 3 are averages, each calculated from a series of individual spectra obtained at the corresponding location. For graphene on Ir(111), our dI/dV data show the existence of a local maximum of around 0.3 eV below the Fermi level, as shown by the dashed-line arrow in Fig. 3(a). This maximum must be related to the Ir(111) surface state, for which a value of 0.4 eV has been reported. This result reveals that interaction between graphene and its underlying substrate is consistent with that found in previous work, where it was reported that the graphene $\pi$ band hybridizes strongly with the Ir 5d state near the Fermi level. With silicon intercalation, this maximum feature is absent (the black spectra). This directly demonstrates that intercalated silicon effectively weakens the interaction between graphene and the Ir substrate. Moreover, without silicon intercalation, we see that the spectrum is asymmetric. After silicon intercalation, the spectrum becomes symmetric. This symmetry resembles intrinsic graphene. Therefore, our data reveals that silicon-intercalated graphene on Ir(111) behaves like intrinsic graphene.

From the foregoing, we can conclude only that for a small area, the quality of graphene after silicon intercalation is almost as good as intrinsic graphene, so we also need to characterize its physical properties from the macroscopic view. As Raman spectroscopy has been widely used in...
characterizing the properties of graphitic materials, we employ it to characterize the physical properties of silicon-intercalated graphene on Ir(111). In order to compare un-intercalated graphene and silicon-intercalated graphene, we obtained Raman spectra of both systems, as the data shown in Fig. 3(b) from the samples of Gr/Ir and Gr/Si/Ir. The Gr/Ir obtained Raman spectra of both systems, as the data shown intercalated graphene and silicon-intercalated graphene, we intercalated graphene on Ir(111). In order to compare un-
employ it to characterize the physical properties of silicon-
Gr/Ir, indicated by the red line in Fig. 3(b), owing to the
intercalation, there is no Raman signal from the sample of
produced between the graphene and the Ir substrate. Before
plus annealing till a large-scale Si-intercalated interface was
Ir(111) substrate, which is in agreement with a previous
study. After silicon intercalation, the two prominent
Raman features of graphene, the G peak and 2D peak, emerge in the curve obtained from the Gr/Si/Ir sample. It is
obvious that the silicon layer effectively decouples the inter-
action between graphene and the Ir(111) substrate. The blue
shift of both the G peak and 2D peak must be caused by a litt-
tle mechanical strain and the charge from the underlying sili-
c. In addition, the absence of a D peak in the curve indicates that the intercalated graphene has nearly no defects. Therefore, combining Raman spectra with dI/dV data discussed above, we conclude that the properties of the silicon-intercalated graphene on Ir(111) are almost the same as those of freestanding monolayer graphene.

In summary, the interfacial properties of silicon-intercalated graphene on Ir(111) substrate have been charac-
terized by LEED and STM. Graphene fabricated on Ir(111) is shown to have a moiré superstructure with a periodicity of 2.5 nm. But after silicon intercalation, a new superstructure emerges with a periodicity of 1.2 nm. The atomically resolved STM image and the corresponding FFT pattern reveal that the topmost graphene layer is intact and continuous after silicon intercalation. Furthermore, high-pass FFT treatment of the image reveals the honeycomb pattern of the underlying silicon layer. By dI/dV spectroscopy, the differences in graphene’s electronic properties before and after silicon intercalation are clearly demonstrated. The influence of the Ir substrate to gra-
phene is effectively weakened by the intercalated silicon, and the corresponding dI/dV spectra become more symmetrical. The vibrational modes of the graphene adlayer after silicon intercalation are also detected in Raman spectroscopy, where G and 2D peaks are visible and the D peak is absent. Our present work shows that the silicon intercalation effectively decouples the interaction between graphene and its Ir(111) substrate. This intercalated silicon serves as a buffer between graphene and its metal host and can facilitate the construction of nanoscale devices based on epitaxially grown graphene.

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