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Intercalation of metal islands and films at the interface of epitaxially grown graphene and Ru(0001) surfaces

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We report on intercalation of seven kinds of metals—Pt, Pd, Ni, Co, Au, In, and Ce—at the interface between an epitaxially grown graphene layer and a Ru(0001) substrate. Atomic resolution scanning tunneling microscopy images of perfect graphene lattice are obtained on top of these intercalated metals, showing that the high quality of the original graphene is, in the end, undisturbed by the intercalation. A model based theoretical calculation is proposed for the intercalation mechanism: metal atom-aided defect formation and self-healing of C–C bonds at high temperature. These intercalated materials include noble metals, magnetic metals, a IIIA group metal, and a rare earth metal, which indicates that intercalation through epitaxial graphene on Ru(0001) is a universal approach for metals. © *2011 American Institute of Physics*.
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Graphene, a two-dimensional sp^2 bonded honeycomb carbon lattice, attracts increasing attention due to its unique structure and outstanding properties.[1] In the last few years, an epitaxial carbon adlayer on single-crystal surfaces has been achieved as a large-area uniform graphene layer with low defect density, which is crucial for extensive application in future devices. Epitaxial graphene on Ru(0001)[2–7] provides a high quality adlayer but has a strong interaction with the substrate, which hybridizes graphene's C π bond and can disturb its unique electronic properties. Previous works have shown that this interaction can be effectively weakened via intercalating a layer of another element, such as Au,[8–10] Ag,[11,12] or Cu,[13] between epitaxial graphene and its substrate, which makes graphene regain its linearly dispersed energy band or even open up a band gap at around the Dirac point.[10] Studies using angle-resolved photoemission spectroscopy (ARPES) and electron-energy-loss spectroscopy (EELS) have found that the intercalated layer effectively decouples epitaxial graphene from the substrate and makes it more like freestanding graphene.[8] Meanwhile, Premlal *et al.*[14] studied gold intercalated in graphene/SiC(0001) by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) and found that different intercalated structures have different impacts on the electronic structure of graphene. These experimental results elucidate the great potential of intercalation to decouple epitaxial graphene from the substrate and also indicate the crucial potential in different intercalated structures for tuning graphene's electronic properties. However, most of the previous investigations of intercalation focus on Au, which is often used as an electrode material in the microfabrication industry, while intercalated structures incorporating other important elements like magnetic elements have seldom been studied. In this paper, we report on STM investigations of intercalations of the noble metals Pt, Pd and Au, magnetic metals Ni and Co, IIIA group metal In, and rare earth metal Ce in graphene/Ru(0001).

Our experiments were performed in an ultra high vacuum (UHV) system with a base pressure of 1×10^{-10} mbar, which is equipped with a commercial STM, low energy electron diffraction (LEED) and Auger electron spectroscopy (AES), metal evaporators, and an electron beam heater. Monolayer graphene was grown on the surface of Ru(0001) by ethylene cracking at 1100 K.[3,6] The quality of the graphene was checked by LEED and STM. A metal—Pt, Pd, Ni, Co, Au, In, or Ce—was deposited onto the graphene/Ru(0001) sample kept at room temperature (RT), and then the sample was annealed to an appropriate temperature to intercalate the metal atoms underneath the graphene. The coverage of all the metals is controlled to be less than one monolayer. All samples were checked by AES to rule out contaminations and then scanned by the STM in constant current mode.

Graphene is corrugated into a moiré pattern on Ru(0001) surface because of lattice mismatch.[15] After intercalation with several kinds of metals including noble metals Pt and Pd and magnetic metals Ni and Co, we found that graphene exhibits the same moiré pattern on the intercalated structures as on Ru(0001), as shown by high resolution STM images in Figs. 1(a)–1(d). These metals can intercalate between graphene and Ru(0001) after annealing at 800 K. The intercalated structures are small islands in a symmetrical triangular shape, with the edges along the same close-packed direction as the graphene moiré superstructure. The apparent heights of these intercalated islands for Pt, Pd, Ni, and Co are 2.88, 2.70, 2.50, and 3.00 Å, respectively, which are similar to or even smaller than a step height of close packed crystal surface of the metals, indicating that these metal islands are composed of a single atomic layer.

The intactness of the graphene lattice after the interaction is checked by atomic resolution measurements at the edge region of the islands. STM images in Figs. 1(e) and 1(f) show the topography of the graphene layers on top of the intercalated Pd and Co islands. From these images, we can find that the lattice of graphene is perfect, without any additional defects, and continuous across the edges of the

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intercalated islands, proving that the intercalation process does not damage the graphene overlayer.

Unlike the above-mentioned four metals, after intercalation of Au, In, or Ce, graphene overlayer shows a superlattice that differs from its moiré pattern on Ru(0001), as the topographic images demonstrated in Fig. 2. Au and In can intercalate between graphene and Ru(0001) after annealing at 500 K [Figs. 2(a) and 2(c)]. The intercalated islands are much larger and lower in density than the ones in Fig. 1. Furthermore, if we increase the coverage, either of these two intercalated metals could eventually form a film with atomic flatness. For the Au intercalated films, the majority of the surface is flat with a height of about 2.78 Å, equal to a single step height of Au(111). As for the case of Indium, the intercalated films show varying heights ranging from monolayer to multi-layers.

The atomic resolution images in Figs. 2(b) and 2(c) show that the graphene lattice is undisturbed and extends continuously across the intercalated and non-intercalated areas. Moreover, compared with the hexagonal lattice in the area without intercalation, graphene on top of the intercalated islands displays a symmetric honeycomb lattice [Figs. 2(b) and 2(d)]. This suggests that the strong interaction between graphene and the substrate has been blocked[16] and that the graphene is more nearly free-standing after intercalation, which is in agreement with previous ARPES studies.[10]

The intercalation of rare earth metal Ce is quite different from all of the metals mentioned above. Instead of annealing to 500 or 800 K, Ce-intercalation happens at RT directly upon deposition on graphene/Ru(0001). Furthermore, a very special structure is formed. As shown in Fig. 2(e), Ce atoms selectively intercalate from the *atop* and *fcc* regions of the moiré structure. After intercalation, the *atop* and *fcc* regions of the graphene moiré pattern have almost the same height and leave the *hcp* region as imbedded holes, quite similar to the geometry of *h*-BN "nanomesh."[17] This result demonstrates that intercalation could form layers with interesting structures that have great potential to influence the superstructure of graphene. Meanwhile, the atomic resolution image of this graphene "nanomesh" shows a perfect lattice without any defects [Fig. 2(f)] and also confirms that the intercalation process of Ce is not damaging for graphene.

For all the seven metals we have tried, graphene's high quality is always preserved during the intercalation process. Since additional defects may introduce unfavorable impacts on graphene, this non-damaging metal-intercalation method demonstrated here might be a convenient and harmless way to tune the electronic properties of epitaxial graphene.

Next we further expound the intercalation mechanism by theoretical calculations. In previous work, Gall *et al.*[18] attributed the intercalation process to defects in graphene. In our experiments, we also found that some intercalated islands locate underneath defect sites of graphene. However, there are still many more intercalated islands just randomly dispersed underneath the perfect graphene layer, seeming as if the penetration has no relationship with defects. To better explain this phenomenon, we did some primary calculations

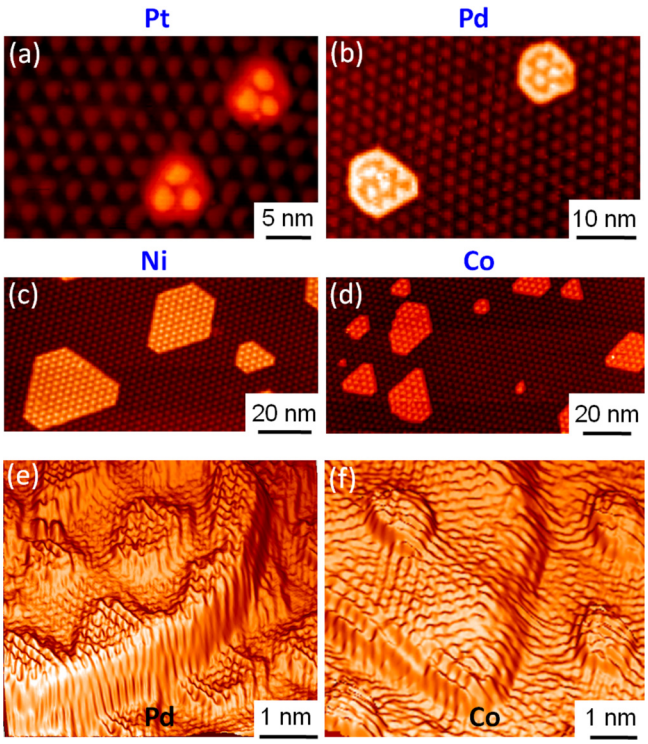

FIG. 1. (Color online) STM topographic images: Pt (a), Pd (b), Ni (c), and Co (d) intercalation structures in graphene/Ru(0001) after annealing at 800 K. (e), (f) Atomic resolution images of graphene on a Pd-intercalated island and a Co-intercalated island, respectively. Scanning parameters: (a) −1.42 V, 0.13 nA; (b) −2.19 V, 0.11 nA; (c) −1.27 V, 0.13 nA; (d) −1.47 V, 0.13 nA; (e) −0.13 V, 2.12 nA; (f) −0.21 V, 1.97 nA.

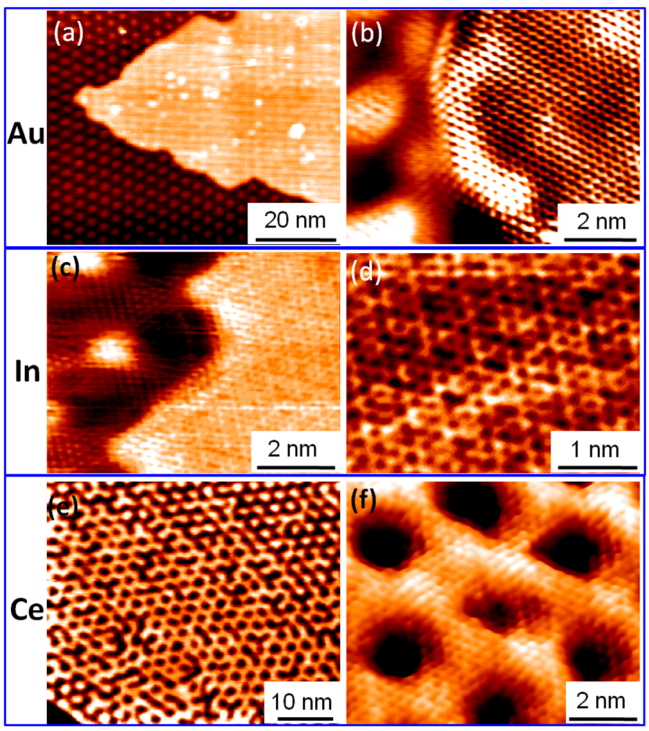

FIG. 2. (Color online) STM topographic images: (a) Au-intercalated structure after annealing at 500 K. (b) Atomic resolution image across an edge of the Au-intercalated film. Graphene shows honeycomb lattice on top of the intercalated film. (c) Indium intercalated at 500 K with atomic resolution of on-top graphene. (d) Zoomed-in image of honeycomb graphene lattice on top of the In-intercalated film. (e) "Nanomesh" structure arising from low coverage Ce-intercalation at RT. (f) Atomic resolution image of graphene on the "nanomesh" structure in (e). Scanning parameters: (a) −2.96 V, 0.05 nA; (b) −0.10 V, 0.40 nA; (c), (d) −0.04 V, 1.34 nA; (e) −0.61 V, 0.12 nA; (f) 0.03 V, 1.16 nA.

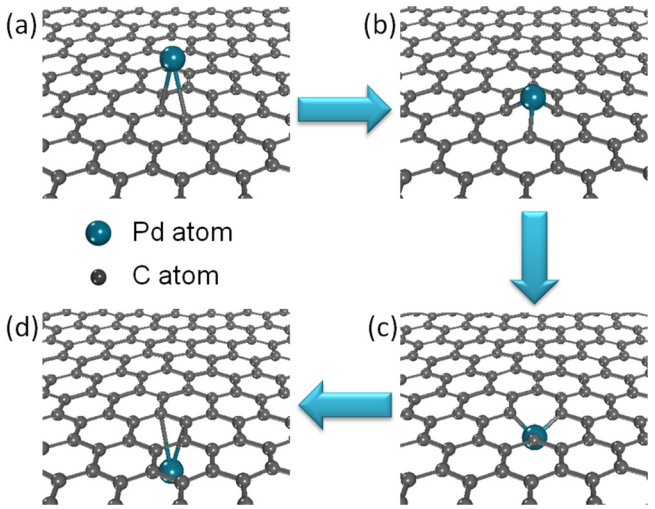

FIG. 3. (Color online) Sketch of the intercalation process of a Pd atom. (a) The Pd atom rests on perfect graphene. (b) At high temperature (800 K), the Pd atom bonds with carbon atoms and induces an atomic defect in graphene. (c) The Pd atom passes through the defect and bonds with the substrate lattice (not drawn here). (d) The carbon atoms re-bond and graphene heals itself.

using the climbing-image nudged elastic band (NEB) method.[19,20] For demonstration, we calculated the energy barrier of a Pd atom through a graphene layer without considering the Ru substrate. First, we used a perfect graphene layer and let the Pd atom go though it by knocking a carbon atom downward and then swapping the two atoms. The calculated energy barrier is 8.66 eV, which is extremely high and unlikely to be overcome. Then we tried to create a single atom defect in graphene and let the Pd atom go through the defect. The energy barrier in this situation is 3.83 eV, which is much smaller than that in the first model. Note that a Pd atom is more stable on Ru(0001) than on graphene (the adsorption energy of a Pd atom is −1.90 eV on graphene and −4.52 eV on Ru(0001), calculated by density function theory (DFT)), we re-calculated the second model (with atomic defect) by taking the substrate into account, and the barrier is lowered to 0.49 eV, which is a very reasonable energy barrier for a Pd atom to overcome.

On the other hand, Pd-intercalation needs annealing to 800 K, at such temperature the thermal vibrations of graphene atoms are more severe and the strength of the C–C bonds is weakened. At the same time, the Pd atoms on top of graphene also vibrate more and have a stronger interaction with the underlying carbon atoms. As sketched in Fig. 3, there are likely opportunities for some C–C bonds in graphene to break and bond with a Pd atom and thus yield locally an atomic scale defect in the graphene lattice. Subsequently, the Pd atoms go through this defect and bond with the Ru substrate since Pd has higher binding energy with Ru, and the carbon atoms would re-bond to each other and heal the graphene lattice. Thereupon, the graphene lattice resumes a pristine state with an underlying intercalated layer while the sample cools down. Using this model of metal-atom-aided-defect-and-self-healing at high temperature in graphene, the intercalations of some metals, like Pd, can be well explained. But for other metals like Ce, which could intercalate at RT, another mechanism should also exist.

In conclusion, seven kinds of metals, Pt, Pd, Ni, Co, Au, In, and Ce, have been successfully intercalated between graphene and Ru(0001) substrate. For all these metals, the graphene layer preserves its perfect atomic lattice after intercalation. The size of graphene moiré superlattice remains the same after intercalation of Pt, Pd, Ni, or Co, but becomes different after intercalation of Au, In, or Ce. We propose a primary model involving metal-atom-aided-defect-and-self-healing of C–C bonds at high temperature to explain the intercalation mechanism of some metals well. The diversity of the intercalated elements and corresponding structures prove that our convenient intercalation method is a universal approach for metals in graphene/Ru(0001) and also has potential for tuning the transport properties of epitaxial graphene for future applications based on it. Our work also provides an efficient way to investigate the physics and the applications of underlying atomic layers and islands of metals with the protection of the stable graphene monolayer.

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