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Fabrication of large-scale graphene/2D-germanium heterostructure by intercalation*

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We report a large-scale, high-quality heterostructure composed of vertically-stacked graphene and two-dimensional (2D) germanium. The heterostructure is constructed by the intercalation-assisted technique. We first synthesize large-scale, single-crystalline graphene on Ir(111) surface and then intercalate germanium at the interface of graphene and Ir(111). The intercalated germanium forms a well-defined 2D layer with a 2×2 superstructure with respect to Ir(111). Theoretical calculations demonstrate that the 2D germanium has a double-layer structure. Raman characterizations show that the 2D germanium effectively weakens the interaction between graphene and Ir substrate, making graphene more like the intrinsic one. Further experiments of low-energy electron diffraction, scanning tunneling microscopy, and x-ray photoelectron spectroscopy (XPS) confirm the formation of large-scale and high-quality graphene/2D-germanium vertical heterostructure. The integration of graphene with a traditional 2D semiconductor provides a platform to explore new physical phenomena in the future.

Keywords: graphene, two-dimensional germanium, heterostructure, intercalation

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1. Introduction

Heterostructures based on graphene and other two-dimensional (2D) materials not only exhibit fascinating properties and potential applications, but also provide new horizons to the research of graphene.[1–4] For example, graphene/h-BN/graphene heterostructures are considered as platforms to study resonant tunneling and negative differential conductivity.[5–7] The combination of graphene with transition metal dichalcogenides (TMDs) overcomes the intrinsic limitations of graphene, offering potential applications in tunneling field-effect transistors (FETs).[8–11] Heterostructures formed by stacking graphene with traditional semiconductors in 2D form have been predicted as promising candidates for tuning the doping of graphene.[12] Among the traditional semiconductors, silicon and germanium have been widely used because of the potential compatibility with current silicon technology. Graphene/silicene heterostructures have been successfully fabricated and exhibit Schottky rectification behavior.[13] Graphene/2D-germanium vertical structure is predicted as a channel material used in switching devices,[14] however, its experimental fabrication has not been demonstrated yet.

A versatile method to construct graphene-based 2D heterostructures is mechanical assembly.[3,15] However, it remains substantially challenging to fabricate the graphene/2D-germanium heterostructure by mechanical assembly due to the absence of a freestanding form of 2D-germanium in nature. Alternatively, intercalation technique based on the epitaxial graphene system brings new opportunities.[16–18] Recently, graphene/2D-silicon heterostructures have been successfully fabricated by silicon intercalation.[13,19] The intercalation technique not only preserves the intrinsic properties of the epitaxial graphene but also takes advantages of its large-scale and high-quality characteristics. Moreover, the graphene layer protects the unstable layer, silicene, effectively. Inspired by these efforts, we aim to fabricate graphene/2D-germanium heterostructure by intercalation technique.

In this work, large-scale, high-quality graphene/2D-germanium (Gr/2D-Ge) vertical heterostructures have been successfully fabricated by the intercalation method. We first grow single-crystalline graphene on Ir(111) surface and then intercalate germanium atoms at the interface of graphene/Ir. The interfacial germanium, which forms a 2×2 superstructure with respect to the Ir(111), has a double-layer structure confirmed by a controlled experiment together with density functional theory (DFT) calculations. The underlying 2D ger-

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manium layer effectively decouples graphene from the Ir substrate, indicating a successful construction of Gr/2D-Ge heterostructures. Scanning tunneling microscopy (STM) shows intact carbon lattices of graphene after intercalation. Low-energy electron diffraction (LEED) patterns and Raman characterizations on the whole sample reveal the large scale characteristic of the fabricated Gr/2D-Ge heterostructures.

2. Methods

Sample preparation and characterizations Graphene growth and germanium intercalation were carried out in an ultra-high vacuum (UHV) system with a base pressure of about 2×10^{-9} mbar. Firstly, the Ir(111) crystal surface was cleaned by repeated cycles of sputtering and annealing (1370 K). Large-scale, single-crystalline single-layer graphene was then fabricated by an oxygen-etching assisted method.[20] Germanium atoms were subsequently evaporated onto the graphene surface at room temperature by electron-beam evaporation, and then the sample was annealed at 750 K for 30 min. STM images were taken at ~ 4 K. LEED was taken with a 4-grid detector (Omicron Spectra LEED) in a connected UHV chamber to identify the superstructure macroscopically. XPS spectra were collected via an ESCALAB 250x XPS microscope using Al $K\alpha$ x-ray source. Raman spectra and maps were obtained by a commercial confocal Raman microscope (WiTec), using an excitation wavelength of 532 nm and power of 2 mW.

First-principles calculations DFT calculations were performed in a plane-wave formulation with the projector augmented wave method (PAW)[21] as implemented in the Vienna *ab initio* simulation package (VASP).[22] The Perdew–Burke–Ernzernhof (PBE)[23] parameterization of the generalized gradient approximation (GGA)[24] was used. The cutoff energy of the plane waves was 400 eV. Three-layer atomic slabs were used to simulate the Ir(111) substrate, with Ge atoms adsorbed on one side. The vacuum layer was about 16 Å. In structural relaxations, the Ir atoms in the bottom layer were fixed, while the upper two layers of Ir atoms and the Ge atoms were totally relaxed until the force on every atom was smaller than 0.01 eV/Å. The k-points sampling was $21 \times 21 \times 1$. The optB86 vdW-corrected exchange–correlation functional was used to account for the vdW interactions.[25,26]

3. Results and discussion

Figures 1(a) and 1(b) show a schematic to illustrate the fabrication procedure of Gr/2D-Ge heterostructure on Ir(111). Large-scale, single-crystalline single-layer graphene is epitaxially grown on a clean Ir(111) crystal surface (Fig. 1(a)). The germanium atoms are deposited onto the surface of the as-grown graphene, and then annealed to initiate the intercalation. The intercalated germanium atoms diffuse at the interface and form a 2D layer beneath graphene (Fig. 1(b)).

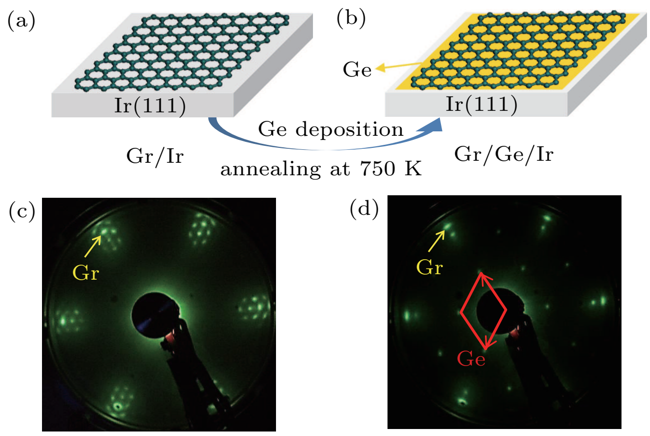

Fig. 1. Fabrication processes of Gr/2D-Ge heterostructures. (a), (b) Schematic of the fabrication processes; (c), (d) LEED patterns of the sample at (a), (b) stages, respectively.

To check the results of each step, we performed LEED measurements for the sample. The LEED pattern of the as-grown graphene on Ir(111) (Fig. 1(c)) shows a set of sharp spots and surrounding satellite spots, which are attributed to the graphene adlayer and the Moiré pattern from the lattice mismatch between graphene and Ir, respectively. No extra diffraction spot from rotational graphene domains indicates that the fabricated graphene is single-crystalline.[20] After depositing germanium followed by annealing process, the LEED pattern changes significantly as shown in Fig. 1(d). The diffraction spots of graphene remain sharp and clear while the satellite spots from the Moiré pattern almost disappear, suggesting a weakened interaction between graphene and Ir(111). Moreover, a new set of diffraction spots exhibiting a 2×2 periodicity with respect to Ir(111) emerge (marked by the red rhombus). We also find that LEED patterns obtained at different locations across the entire sample show the same feature. These results indicate that the Ge atoms are intercalated at the interface between graphene and Ir over a large area.

To investigate the atomic structure after germanium intercalation, we performed STM measurements. A large-scale STM image of the as-fabricated graphene (Fig. 2(a)) shows a defect-free Moiré pattern with a periodicity of about 2.51 nm. The corresponding unit cell is labeled by a black dash rhombus. The atomically resolved STM image (Fig. 2(b)) clearly shows the honeycomb lattices of graphene. After depositing germanium and annealing, the graphene Moiré pattern becomes very weak (labeled by black dash rhombus in Fig. 2(c)). In addition, a superstructure with a periodicity of 0.54 nm emerges. The direction of this superstructure is aligned with the direction of Ir(111) and its periodicity of 0.54 nm is about two times of the lattice constant of Ir(111) (0.27 nm), indicating a 2×2 periodicity with respect to Ir(111). The high resolution STM image in Fig. 2(d) shows a flat honeycomb structure of the topmost graphene without Moiré pattern. These results indicate that the germanium atoms have been successfully intercalated below graphene and form a well-defined crystalline structure. Moreover, the graphene keeps its high-quality after the intercalation of germanium.

To further confirm the formation of graphene/germanium heterostructure and characterize the quality of graphene, we carried out x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Before intercalation, the spectrum shows no germanium signal. After intercalation, the Ge 3d peak emerges and exhibits two narrow components due to the spin–orbit splitting, as shown in Fig. 3(a). The Ge 3d peak is around 29.1 eV, indicating that the interfacial germanium is in elemental state rather than Ir germanide.[27] XPS spectra of C 1s centered around 284.1 eV (Fig. 3(b)) for graphene before and after the formation of graphene/germanium heterostructure show characteristic features of sp^2-hybridized carbon. The slight downshift (about 0.12 eV) implies a weak p-doping in the graphene after Ge intercalation. A similar p-doing effect was reported in a graphene on SiC after Ge intercalation.[28,29]

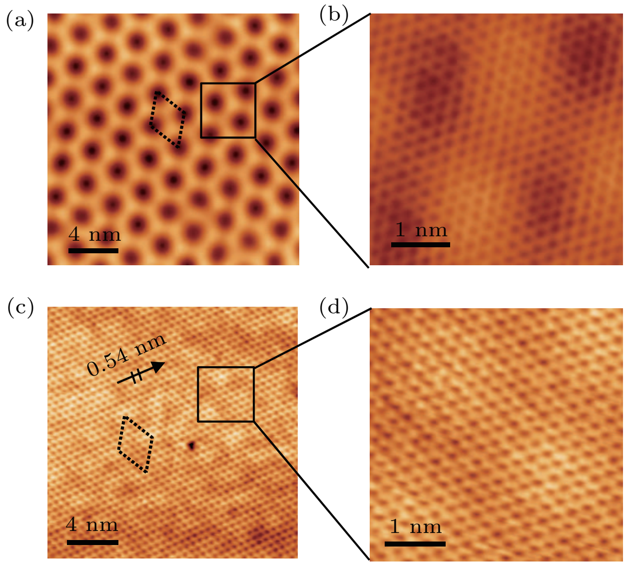

Fig. 2. STM characterizations for sample before and after Ge intercalation. (a) A large-scale STM image ($U = -1.54$ V and $I = 0.05$ nA) of the as-fabricated graphene on Ir(111). The unit cell of the graphene Moiré structure is labeled by dash rhombus. (b) An atomically resolved STM image ($U = -0.05$ V and $I = 0.3$ nA) showing honeycomb lattices of the graphene. (c) A large scale STM image ($U = -1.5$ V and $I = 0.1$ nA) of the sample after germanium intercalation. The dash rhombus labels the weak graphene Moiré pattern. A new structure with a periodicity of 0.54 nm is visible. (d) An atomic resolved STM image ($U = -0.01$ V and $I = 20$ nA) of the Ge intercalated graphene.

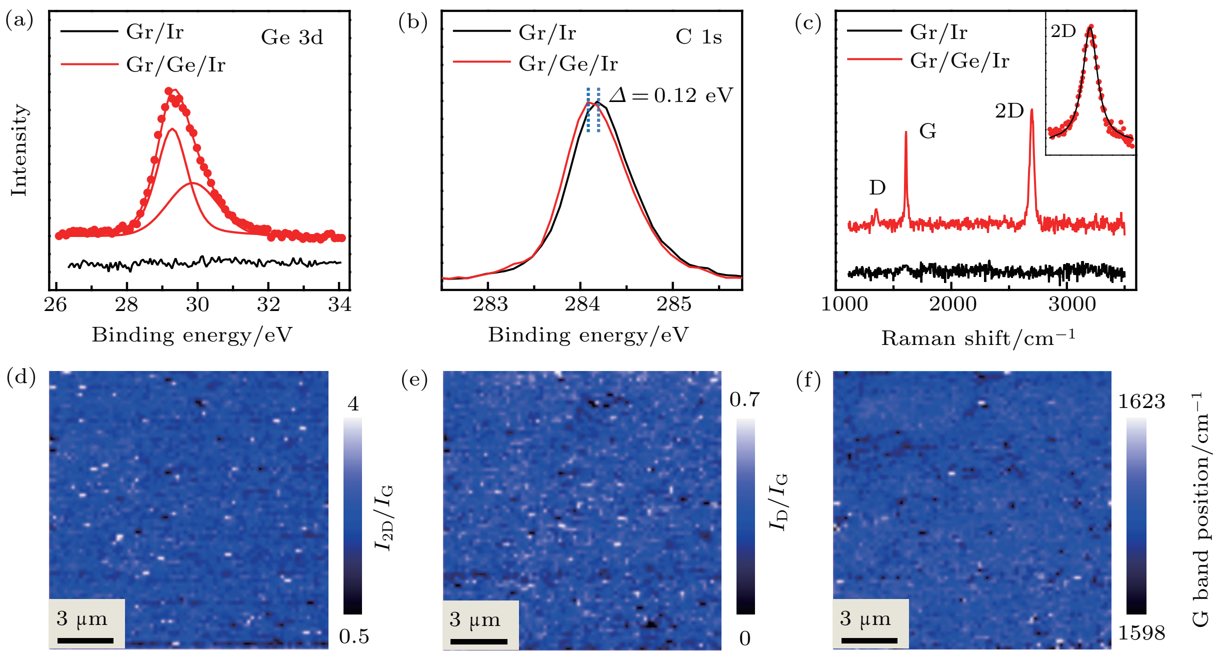

Fig. 3. XPS and Raman measurements for the samples before and after Ge intercalation. (a) Ge 3d core-level spectra of Gr/Ir (black curve) and Gr/Ge/Ir (red curve) samples. (b) C 1s core-level spectra of Gr/Ir (black curve) and Gr/Ge/Ir (red curve) samples. (c) Raman spectra of graphene before (black curve) and after (red curve) Ge intercalation. Inset is the 2D band of the graphene after intercalation, well fitted by a single Lorentzian peak. (d)–(f) Raman maps of the intensity ratio of 2D to G bands (I_{2D}/I_G), intensity ratio of D to G bands (I_D/I_G), and positions of G band for Ge intercalated graphene, respectively.

We also check the Raman spectra of the graphene before and after germanium intercalation, as shown in Fig. 3(c). The as-prepared epitaxial graphene on Ir shows no detectable Raman signals due to the strong hybridization between graphene π-band and the Ir substrate.[30] After the Ge intercalation, the appearance of the characteristic Raman features of graphene suggests that the intercalated Ge layers effectively decouple graphene from the Ir substrate, which is in agreement that the intercalation materials protect the Dirac Fermions of graphene.[12,17] Figures 3(d)–3(f) are large-scale Raman maps

(15 μm ×15 μm) of the intensity ratio of 2D to G peaks (I_{2D}/I_G), the intensity ratio of D to G peaks (I_D/I_G), and positions of G peak, respectively. The 2D peak is well fitted by a single Lorentzian peak with full-width at half-maximum (FWHM) of ∼ 42 cm^{-1} (inset in Fig. 3(c)) and the average value of I_{2D}/I_G is around 1.7, suggesting that the graphene is single layer.[31] The I_D/I_G has a small value of about 0.35 over large areas, indicating a high quality of graphene after intercalation. Besides, the homogeneous distribution of the G peak for the intercalated graphene reflects the uniformity of the intercalated germanium layer. Raman characterizations together with LEED and STM measurements give strong evidence that we have successfully fabricated large-scale and high-quality graphene/2D-germanium heterostructures.

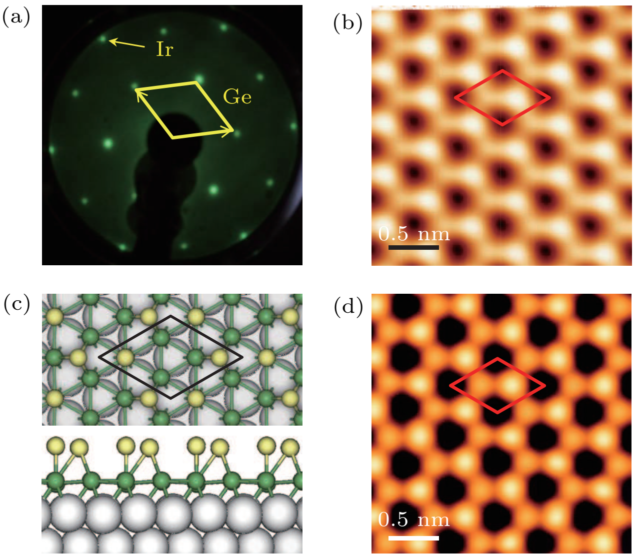

Fig. 4. Structure of the 2D germanium on Ir(111). (a) A LEED pattern of the 2D germanium on Ir(111). (b) A corresponding STM image with atomic resolution ($U = -1$ V and $I = 20$ nA). (c) Top and side views of the relaxed atomic model of a double-layer Ge on Ir(111). (d) A simulated STM image for the configuration in (c), which is in nice agreement with the STM image in (b).

To investigate the detailed structure of the intercalated 2D germanium at the interface, we performed a control experiment, i.e., directly depositing Ge atoms on the clean Ir(111) surface followed by annealing to 750 K for 30 min (the same condition to the Ge intercalation experiment). Without graphene layer on the top, germanium on the Ir(111) surface also forms 2×2 superstructure with respect to Ir(111) lattice, as shown in the LEED pattern in Fig. 4(a). The corresponding STM image in Fig. 4(b) shows uniform hexagonal morphology with a periodicity of 0.54 nm. With the help of DFT calculations, we find that the configuration of the as-fabricated Ge on Ir(111) is a double-layer structure, as shown in Fig. 4(c). The Ge atoms in the bottom layer, one monolayer, sit at the hollow sites of the Ir(111) surface. The top layer is 1/3 monolayer, in which there are two groups of Ge atoms sitting at the top and hollow sites of the bottom layer, respectively. The Ge atoms at atop sites are about 0.12 Å higher than those at hollow sites. The STM simulation in Fig. 4(d) shows hexagonal morphology, in good agreement with the zoom-in experimental STM image in Fig. 4(b).

4. Conclusion

We successfully fabricate a large-scale and high-quality graphene/2D-germanium heterostructure by intercalation technique. Graphene is firstly grown on Ir(111) surface by molecular beam epitaxy. Then, Ge atoms are intercalated at the interface between the graphene and Ir substrate, which forms a crystalline 2D layer, implying a successfully construction of graphene/2D-germanium vertical heterostructure. A controlled experiment by depositing germanium directly on Ir(111) together with first-principles calculations finds that germanium on Ir(111) is in a 2D form. LEED, STM, and Raman characterizations show that intrinsic properties of graphene are preserved after intercalation, confirming the large scale and high quality of the fabricated graphene/2D-germanium heterostructures. This study paves a way to further explore the new physics and potential applications based on graphene/2D-semiconductor heterostructures.

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