Spectroscopic and scanning probe analysis on large-area epitaxial graphene grown under pressure of 4 mbar on 4H-SiC (0001) substrates*

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We produced epitaxial graphene under a moderate pressure of 4 mbar (about 400 Pa) at temperature 1600 °C. Raman spectroscopy and optical microscopy were used to confirm that epitaxial graphene has taken shape continually with slight thickness variations and regularly with a centimeter order of magnitude on 4H-SiC (0001) substrates. Then using X-ray photoelectron spectroscopy and Auger electron spectroscopy, we analyzed the chemical compositions and estimated the layer number of epitaxial graphene. Finally, an atomic force microscope and a scanning force microscope were used to characterize the morphological structure. Our results showed that under 4-mbar pressure, epitaxial graphene could be produced on a SiC substrate with a large area, uniform thickness but a limited morphological property. We hope our work will be of benefit to understanding the formation process of epitaxial graphene on SiC substrate in detail.

Keywords: SiC substrate, graphene, epitaxial graphene

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1. Introduction

Graphene, a mono-atomic (or a few atomic layers of) carbon with a form of sp^2 at room temperature was isolated experimentally in 2004.[1] As the thinnest and lightest material people can make presently, graphene has exhibited extremely novel and intriguing electronic, thermal, mechanical, optical, chemical, and physical properties,[2] so a "gold rush" has been ignited including theoretic, experimental, applicative fields, and others.[3–9] However, how to produce a large uniform, homogenous, and controlled number thickness wafer-size graphene film is still a very difficult problem. In fact, graphene represents a kind of much more complex material, including different layer types of graphene, such as mono-, bi-, tri-, few-layer graphene (up to about ten layers), and so on. What is more, graphene produced by different methods have many different properties.[10,11] At present, there are many methods for fabricating graphene, among which the three main methods are as follows: (i) chemical vapor deposition (CVD) of a thin carbon atom sheet on single-crystal metal substrates such as cooper, nickel, and so on; (ii) micromechanical exfoliation (or the "scotch tape" technique) of highly oriented pyrolytic graphite (HOPG) crystal; (iii) graphene grown epitaxially on silicon-terminated (0001) or carbon-terminated $(000\bar{1})$ semi-insulating 4H-, 6H-SiC, or cubic-SiC(001)/Si(001) or 3C-SiC substrates by solid-state thermal decomposition process of silicon at high temperature.[10–16] As it is easily compatible with current semiconductor processing technology and a method for large-scale production of graphene, the last technique is regarded as one of the most promising potions for making graphene-based devices, wafer-scale graphene integrated circuits and others.[3–5,17] There are many factors affecting the formation of epitaxial graphene on SiC substrates, such as the surface structure of the substrate, the growing pressure, temperature, time, and so on. The formation mechanism and thermal dynamics of this process is not yet understood theoretically. Former researches on epitaxial graphene mainly focused on the formation mechanism under the conditions in an ultra high vacuum (UHV) (pressure$< 10^{-8}$ Pa) or an argon atmospheric pressure.[18–23] Samples produced under the UHV condition have a small size with a low quality; under the argon atmospheric environment, samples have a high quality at the cost of hoisting the formation temperature. However, the formation of epitaxial graphene under a middle-pressure condition is seldom noticed. In this paper, we fabricated epitaxial graphene under an argon partial pressure of about 4 mbar in the growing process for controlling the Si atoms sublimating from the SiC substrate, and analyzed its morphology properties and chemical compositions of carbon atoms on the substrate. Comparing it with epitaxial graphene under UHV or an argon atmospheric condition theoretically and experimentally, we conclude that epitaxial graphene can also be grown under moderate pressure and our method is a new and reasonable way to produce epitaxial graphene.

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2. Experimental techniques

4H-SiC (0001) substrates (obtained from CREE Research Inc.) were used as epitaxial growth surface with 8° off-axis mis-orientation toward the [11$\bar{2}$0] direction and n-type nitrogen concentration 10^{18} cm^{-3} or so. SiC samples were cut into 1 cm × 1 cm squares from the wafer (2-inch in diameter) and then were pre-cleaned with a standard RAC chemical cleaner to remove the surface contaminants. There was residual scratch damage on the surface of the as-received substrate as shown in Fig. 1, which is harmful to the formation of epitaxial graphene, so a hydrogen-etching process was carried out at 1600 °C for 90 minutes in order to remove this damage, leaving an ordered step-terrace atomically flat arrangement on the surface of the SiC substrates. An atomic force microscope (AFM) measurement was carried out to scan the morphological character, as shown in Fig. 2, we can see that the typical terrace width is about a few microns, and the step height is a few nanometers. After that, SiC samples were entered into the chamber (the base pressure is no less than 1×10^{-5} Pa) of an Aixtron/Epigress VP508 hot-wall chemical vapor deposition reactor, the epitaxial growth process was implemented under a low argon-pressure 4 mbar at the temperature 1600 °C. Finally, samples were cooled down to room temperature in an argon condition overnight.

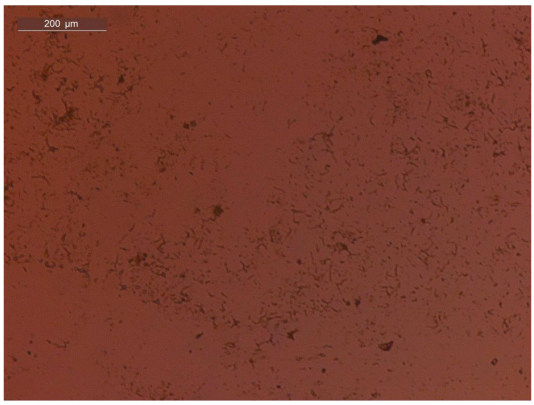


Fig. 1. (color online) The surface morphologies of Si-face of 4H-SiC substrate characterized by Nomarski interference contrast microscopy before hydrogen-etching.

We used a micro-Raman spectrometer (JYHoriba LabRAM spectrometer) excited by the 514.5 nm (2.41 eV) visible beams from an Ar^+ laser to detect the Raman properties of different regions on the surface of the SiC substrate at room temperature and an ambient pressure. The diameter of the laser spot is 500 nm and the spot size of the computer software interface 100X. Before measurement, the Raman spectroscopy system was calibrated using a Si sample with 520 cm^{-1} band. X-ray photoelectron spectroscopy (XPS: Thermo Scientific MSC-Advantage system, a non-monochromatic Al K-alpha X-ray ($h\nu = 1486.6$ eV) source with a residual pressure of 10^{-8} Pa) was performed to monitor the surface chemical compositions and the bonding of carbon atoms on the as-deposited flake. Auger electron spectroscopy (AES) was detected by a PHI660 (physical electronic Inc.) under the working voltage 5 kV and currency 100 nA. Finally, an AFM and a scanning force microscopy (SFM: Seiko, SPI3800-SPA-400) were used to investigate the surface morphological properties.

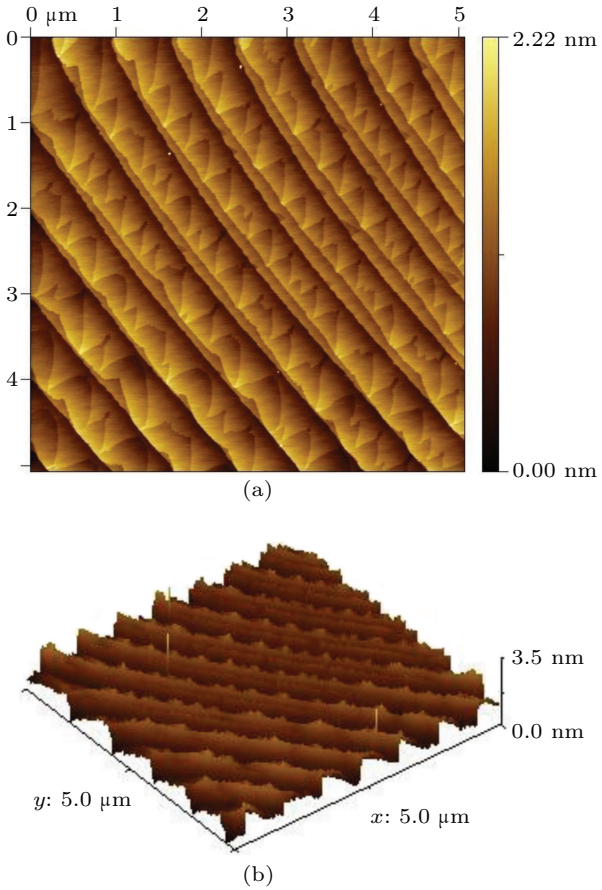


Fig. 2. (color online) Typical AFM height images of (a) two-dimensional, (b) three-dimensional on 4H-SiC (0001) substrate after hydrogen-etching in the zone 5 μm × 5 μm.

3. Results and discussion

In the optical micrograph, there are three typical domains with different brightnesses such as light grey, grey, and black on the surface of the substrate as shown in Fig. 3. Subsequently, Raman spectra were carried out to investigate those locations above, representative spectra of different domains together with that of the bare SiC substrates for reference are shown in Fig. 4, from which we can see that there are five main Raman bands in the range from 1200 cm^{-1} to 3000 cm^{-1}, their names and material origins are shown in Table 1 in detail. From Fig. 4, we can confirm that epitaxial graphene has taken shape on the surface of the substrate because a G band (1584 cm^{-1}) and a two-dimensional band (about 2712 cm^{-1}) appeared simultaneously. The relative intensities of the G and the 2D bands from those three different domains above show that few-layer graphene has grown on the substrates. Those three different domains were turned to correspond to different layer thicknesses of epitaxial graphene due to their analogous Raman spectra, so there is a correlation between the brightness and the thickness caused by the interference with local thickness variations of epitaxial graphene and SiC substrate.

Graphene in the black region is thicker than that in the grey and light grey regions; the grey region covers the majority of the surface with a larger size. By subtracting the bare SiC Raman signal from the graphene/SiC substrate, we got the Raman spectroscopy of epitaxial graphene (grey region) on the surface of the substrate as shown in Fig. 5. After a simple calculation, the full-width at half-maximum (FWHM) of the 2D band 81 cm^{-1} and using formula[24]

$$\text{FWHM (2D)} = (-41/N + 92)\ \text{cm}^{-1}, \quad (1)$$

we get approximately the layer number of the epitaxial graphene $N = 4$. Due to the fact that the 2D band can be fitted with a two-Lorentzian function (as shown in the inset of Fig. 5), and the FWHM of the G band is 22 cm^{-1}, which is in good agreement with the four-layer graphene on SiC (0001) mentioned in the previous work,[25] so we determine that the thickness of epitaxial graphene is four layers. Although there is thickness variation, the thicknesses of the layers are very similar, so our epitaxial graphene is uniform in thickness, which entirely covers the whole surface of the substrate. The redshift of the 2D band shown in Fig. 4 from curve b to curve d suggests that the layer number increases the tensile stresses on the surface. Moreover, the shape and position of the Raman spectra reveal epitaxial graphene with an A–B stacking.[25–28]

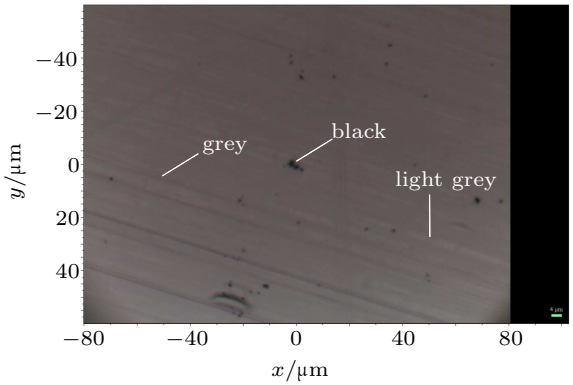


Fig. 3. Wide range of typical optical micrograph of light grey, grey, and black regions used for Raman characterization of large-area epitaxial graphene.

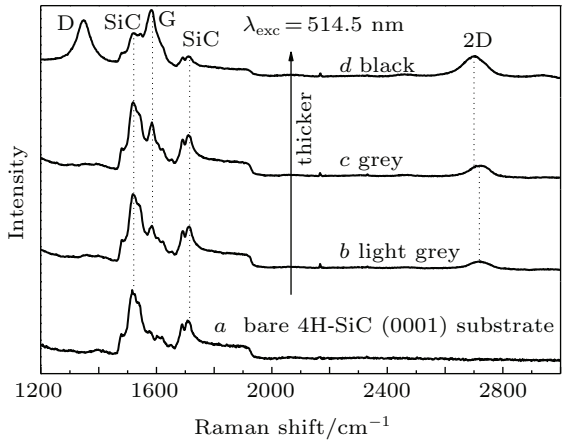


Fig. 4. Raman spectra measured from the bare 4H-SiC (0001) substrate (curve *a*), epitaxial graphene with light grey (curve *b*), grey (curve *c*), and black regions (curve *d*). In the frequency region, the G peak is overlayed by strong multi-phonon signals from the SiC substrate. All those Raman data were normal.

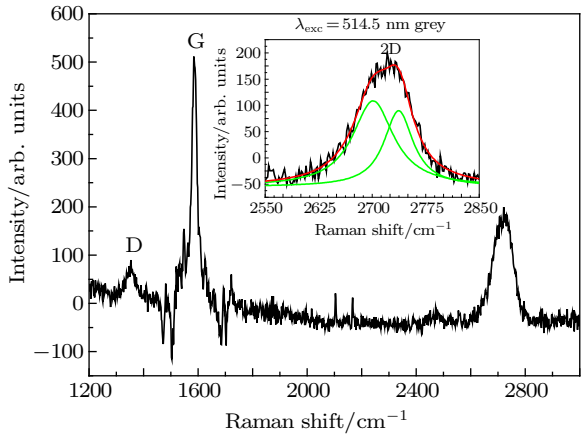


Fig. 5. (color online) Raman spectrum of epitaxial graphene measured from the grey domain. Inset shows that the 2D band can be fitted with a two-Lorentzian function. The shape and position reveal four-layer graphene.

Table 1. Raman spectroscopy bands for graphene/SiC substrate.

Band position/cm^{-1}	Band name	Material origin
1354	D (LO phonon)	graphene
1519	TO phonon	SiC
1584	*G* (Γ point TO and LO phonon)	graphene
1712	*L* point optical phonon	SiC graphene
2712	2D (*K* point iTO phonon	graphene

The defect-induced D band (1354 cm^{-1}), which cannot appear in ideal graphene, suggests that the pristine graphene symmetry is broken by edges or defects. The peak intensities ratio between D and G bands can be used to estimate the domain size of epitaxial graphene.[29] The domain size of the epitaxial graphene in our work is about 94.3 nm.

In order to detect the spatial uniformity of the graphene film, we implemented a measurement for two-dimensional Raman mapping of the 2D band position of epitaxial graphene on 4H-SiC (0001) substrate as shown in Fig. 6. The scanning was performed with 200 ms/point and at every 1 μm over an area of 10 μm × 10 μm. Figure 6 shows that there is a non-uniformity local thickness variation in the graphene layer.

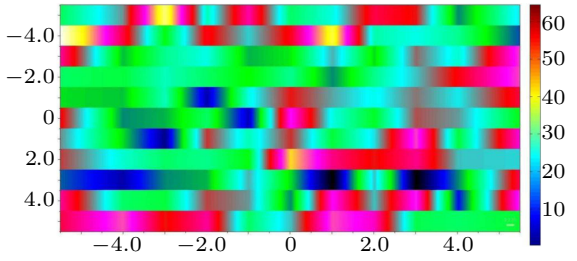


Fig. 6. (color online) Two-dimensional Raman mapping of the 2D band position of epitaxial graphene on 4H-SiC (0001) substrate, the scales of the *x* axis and *y* axis are micron.

Figure 7 shows the C 1s core-level spectroscopy taken from the epitaxial graphene grown on the substrate at a photoemission angle of 0°. The band at a binding energy (BE) of 284.58 eV is associated with the non-oxygenated carbon atoms, which is sp^2-bonded graphitic carbon located on the surface of the substrate.[30,31] It is obviously shown that the

majority are sp^2-hybridized carbon atoms, which keep a high percent compared with the number of C in the Si–C bonds, so we may deduce that epitaxial graphene was produced across the surface of the substrate. Moreover, the sp^3-hybridized carbon in C–OH at 286.37 eV is the result of carbon exposed to air, and carbon bound silicon in Si–C at 282.71 eV corresponds to the SiC substrate.[32]

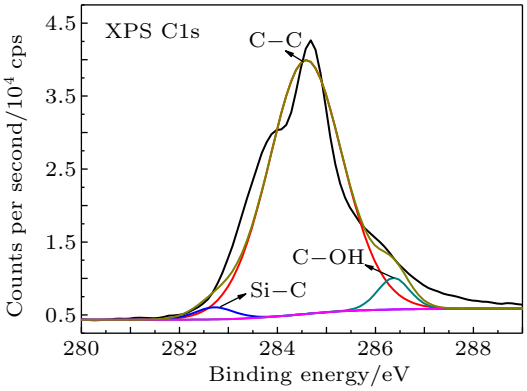


Fig. 7. (color online) The C 1s core-level XPS of epitaxial graphene on the substrate. XPS data were deconvoluted into three bands of Si–C, sp^2, and C–OH.

Auger electron spectroscopy is a nondestructive core-level electron spectroscopy for semi-quantitative determination of the element composition present on the solid surface and also a tool for estimating the layer thickness of epitaxial graphene by modeling the ratio of the measured intensities in the Si (92 eV) and C (272 eV) Auger peaks.[10,11] The carbon AES spectra from 50 eV to 550 eV give a significant change tendency from C in SiC to C in (light grey, grey, and black regions) epitaxial graphene as shown in Fig. 8. We found the following: (i) the ratio of Auger Si to C of SiC substrate is 6.7, which is in good agreement with the result in Refs. [10]–[11]; (ii) Si or O Auger intensity decreases weaker and weaker as the epilayer becomes thicker and thicker, the C:Si ratio changes from 7.8, 9.8, to 10.3, which correspond to about four-layer epitaxial graphene,[33] it is well consistent with the results of Raman spectroscopy; (iii) the number of carbon atoms per 100 atoms increase from 52.2, 57.7, 59.9 to 63.6, the number of silicon and oxygen atoms decrease from 30.3, 35.2, 32.2 down to 27.2 and from 17.6, 7.3, 7.9 down to 9.1 respectively, which demonstrates the thicker epilayer graphene.

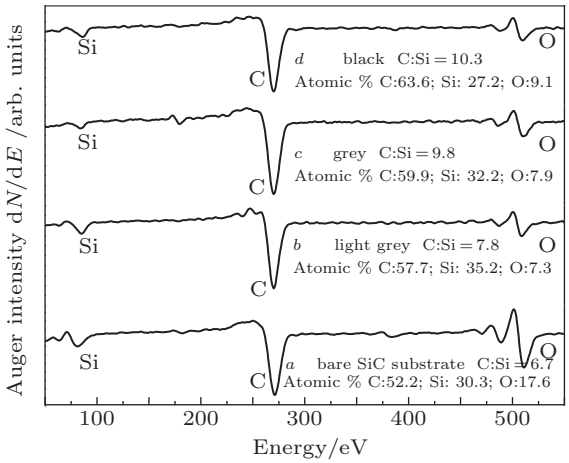


Fig. 8. Auger peak-to-peak ratio of Si (LVV)/C (KLL) lines for 4H-SiC (0001) substrate (curve *a*), epitaxial graphene (curve *b*, curve *c*, and curve *d*) acquired from the surface locations indicated in Fig. 1.

Subsequent AFM and SFM techniques were implemented to study the surface morphology of epitaxial graphene on the substrate in detail as shown in Figs. 9 and 10. We observed that a large continuity of epitaxial graphene has taken shape along the extended terraces and step bunches with a width about 0.4 microns and a height variation of about 30 nm in the direction orthogonal to the step over all the samples, which is well consistent with the results in Ref. [34]. It is necessary to note that the surface height variation does not mean the graphene thickness variations. Although multi-layer graphene formed with a rough morphology under this condition is partly the result of the large step density of the 8° off-axis SiC substrate,[35] our epitaxial graphene has a need-to-improve morphological quality.

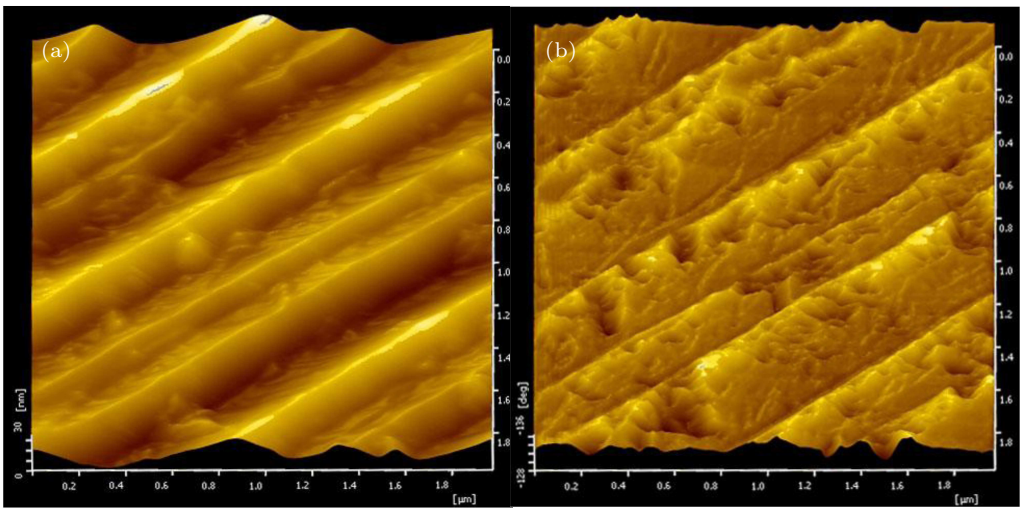


Fig. 9. (color online) AFM images of (a) topographical image, and (b) phase image from the same region of epitaxial graphene with a size of 2 μm × 2 μm on the Si-face (0001) 4H-SiC substrate.

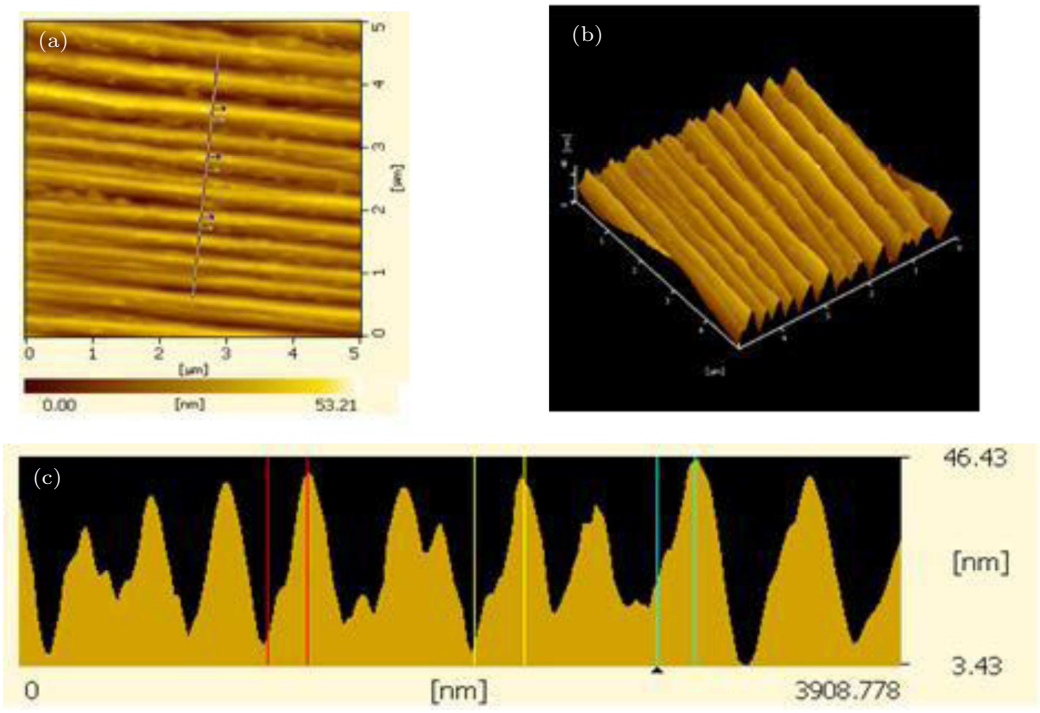


Fig. 10. (color online) Typical SFM height images of (a) two-dimensional, (b) three-dimensional, and (c) linescan in the direction orthogonal to the step of epitaxial graphene grown on 4H–SiC (0001) substrate in the zone in 10 μm × 10 μm .

4. Discussion

Qualitative analysis on the formation of epitaxial graphene grown on a SiC substrate under a moderate pressure environment is as follows. Epitaxial graphene grown on a SiC substrate is a Si-sublimation process followed by a C-graphitization process, which releases Si from the Si–C bond and leaves C self-organization in the form of a sp^2 C–C bond. Under UHV conditions, the Si atom has an over-quick sublimating rate, which holds back the C rearranged hexagonal lattice, so epitaxial graphene has a lower formation temperature and a small size; in the argon atmospheric environment, Si has an over-large pressure and is hard to sublimate from the SiC substrate, at the cost of hoisting the formation temperature accordingly. While appropriate pressure (i.e., an argon partial pressure of 4 mbar) can adjust the balance of the rates of Si sublimation and C re-construction, which leads to graphene growing easily. As we know, C is found in many forms in nature, such as sp, sp^2, sp^3, and so on, all those forms of C can transfer the form of sp^2 as temperature increases. Moreover, the high temperature is helpful to improve the morphology of epitaxial graphene. Therefore, although the epitaxial graphene we produced under 4 mbar has a limited quality in morphology, our method is a feasible way to fabricate higher quality epitaxial graphene under an argon atmospheric environment if raising the growth temperature.

5. Conclusions and future work

We demonstrated the feasibility of preparing epitaxial graphene films on the Si-face of 4H-SiC substrate under a low argon-pressure condition of 4 mbar at 1600 °C. Using various spectroscopic and scanning probe techniques, we studied its structure and morphology. The morphology is slightly rough, which inevitably degrades the electronic properties of graphene, so how to reveal the formation mechanism under the moderate pressure quantitatively and improve the rough surface morphology of Si-face graphene is our next work.

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