Raman analysis of epitaxial graphene on 6H-SiC (000$\bar{1}$) substrates under low pressure environment*

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Abstract: This article investigates the formation mechanism of epitaxial graphene on 6H-SiC (000$\bar{1}$) substrates under low pressure of 2 mbar environment. It is shown that the growth temperature dramatically affects the formation and quality of epitaxial graphene. The higher growing temperature is of great benefit to the quality of epitaxial graphene and also can reduce the impact of the substrate for graphene. By analyzing Raman data, we conclude that epitaxial graphene grown at 1600 ℃ has a turbostratic graphite structure. The test from scanning electron microscopy (SEM) indicates that the epitaxial graphene has a size of 10 μm. This research will provide a feasible route for fabricating larger size of epitaxial graphene on SiC substrate.

Key words: epitaxial graphene; Raman spectroscopy; turbostratic graphite; SiC
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1. Introduction

Graphene, a single atomic layer of flat graphite, has attracted much interest due to its outstanding electrical, physical, thermal, and chemical properties[1]. Graphene was regarded as one of the candidate materials, aiming at breaking the physical limits effect of Si technology and extending Moore's law in the post-CMOS era[2]. Therefore, investigating a feasible route of producing graphene in a large size with low impurities and defects is an important and valuable topic.

At present, there are three main methods for fabricating graphene, i.e., the chemical vapor deposition (CVD) growth of carbon on metals, exfoliation of highly oriented pyrolytic graphite (HOPG) and epitaxial graphene grown on silicon carbide (SiC) substrate. As is easily compatible with the current CMOS technology, epitaxial graphene has been the focus of much attention for making graphene-based devices[3,4]. However, there are many factors affecting the formation of epitaxial graphene on SiC substrate, such as the type of substrate, the surface structure of substrate, the growing pressure and temperature and time[3]. Former experiments mainly fabricated epitaxial graphene under ultra high vacuum (UHV)[5−8] and argon atmospheric pressure conditions[9]. Epitaxial graphene made in UHV condition has only a size of 100 nm at most[10]; under argon atmospheric pressure conditions, samples are of a higher quality with much larger domain sizes, but the formation temperature will be increased accordingly[9], so this unquestionably adds the cost of preparing graphene. In this paper, we fabricated epitaxial graphene under low pressure on SiC substrate, hoping to get larger size and higher quality epitaxial graphene.

2. Experimental details

In our research, 6H-SiC (000$\bar{1}$) substrate with n-type nitrogen concentration about 10^{15} cm^{-3} was used as epitaxial growth surface. Substrates were pre-cleaned to remove surface contaminants with standard RAC chemical treatments before entering in the chamber of Aixtron/Epigress VP 508 hot-wall chemical vapor deposition reactor. Hydrogen-etching was carried out at 1600 ℃ with a flux of 60 standard liters per minute for removing the polishing damage of SiC substrates. Using an alternating current (AC) mode atomic force microscopy (AFM: Agilent 5500), a regularly uniformly stepped surface with a root mean square roughness of the height 4.21 Å on the SiC (000$\bar{1}$) substrates has been observed as shown in Fig. 1. In the following, reducing temperature and flowing Si flux are used to improve the morphological structure. At last, growth process was implemented under low pressure of 2 mbar at temperatures range from 1400 to 1600 ℃.

We used micro-Raman spectrometer (Renishaw inVia Raman microscope) excited by the 514.5 nm (2.41 eV) visible laser beam from He–Cd laser, to confirm the formation of epitaxial graphene and to analyze their properties. Before measurement, we calibrated Raman spectroscopy system using 520 cm^{-1} band of Si sample at room temperature. For preventing epitaxial graphene from damaging by laser-induced heating, the incident power injected on top of the samples is as low as below 2 mW. Scanning electron microscopy (SEM: JEOL JSM-6390A) was used to observe the size of epitaxial graphene.

Raman spectroscopy provides a nondestructive, fast and informative tool for identifying and characterizing carbon-

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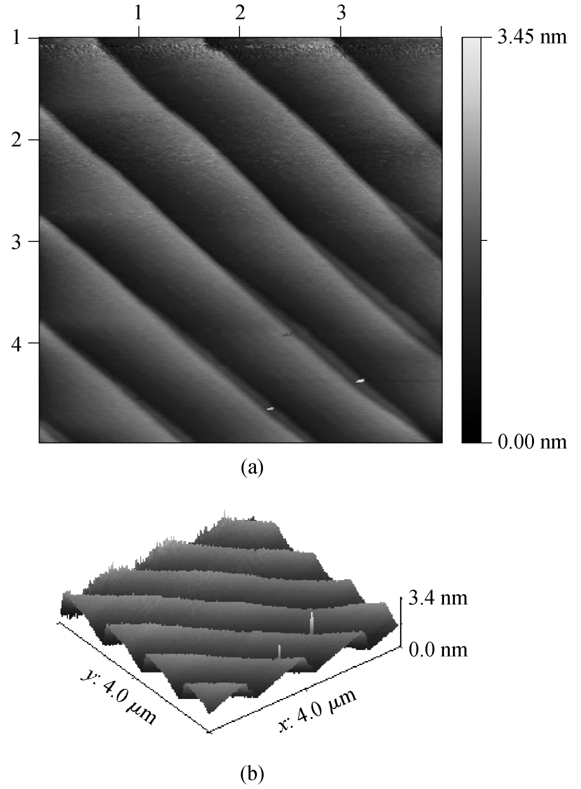

Fig. 1. Typical AFM height images of (a) two-dimension, (b) three-dimension on 6H-SiC (000$\bar{1}$) substrate after Hydrogen etching in the zone 4 × 4 μm^2.

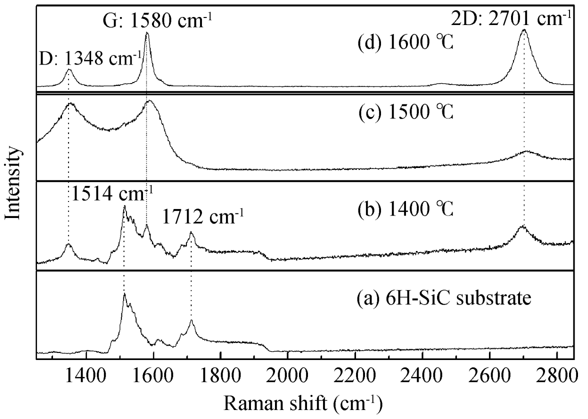

Fig. 2. Raman spectroscopy at excitation wavelength 514.5 nm for epitaxial graphene grown on 6H-SiC (000$\bar{1}$) under low pressure of 2 mbar at different temperatures. From (b) to (d), temperatures increase from 1400 to 1600 ℃, and Raman raw data is normalized.

based materials. The main primary features of epitaxial graphene on SiC substrates in Raman spectroscopy are the so-called G and 2D band. The G band (around 1580 cm^{-1}) is originated from the first order Raman scattering process, it is the characteristic of sp^2 hybridization and involves the in-plane optical phonon (iTO and LO) the two-fold degenerate E_{2g} mode at the first Brillouin zone (FBZ) centre of the phonon band structure. The 2D band (around 2700 cm^{-1}) is a second-order D band due to two phonons (iTO) with opposite momentum in the highest optical branch near the Dirac point K (A'_1 symmetry)[11]. It is fingerprint of mono- or few-layer graphene with electronic properties of massless Dirac fermions and indicates that it is a sign of few-thinner layer structure grown on substrates[12, 13]. The disorder-induced D band (around 1350 cm^{-1}) often appears in Raman spectroscopy, it corresponds to the process of double-resonant excited phonons (LO phonon) in the edge of FBZ, which is sensitive to domain size, the disorder and edges defects in the lattice structure[14].

3. Measurements and results

Figure 2 is Raman spectroscopy of epitaxial graphene samples grown on 6H-SiC (000$\bar{1}$) under 2 mbar pressure conditions at different temperatures 1400, 1500 and 1600 ℃. It is evident that epitaxial graphene has already formed on substrates at temperature above 1400 ℃, which links with the appearance of G and 2D bands simultaneously. At 1400 ℃,the intensities of 1514 cm^{-1} band and 1712 cm^{-1} band, which come from SiC substrates[15], are almost stronger than that of the G band's, this shows that the graphitization process of C atoms has occurred initially, graphene has only a small size with thick layers. Increasing the temperature to 1500 ℃, the graphitization process dramatically shaped, graphene continues growing on substrates in larger sizes with some imperfect lattice because of the advent of D band in Raman spectroscopy. When the temperature increases to 1600 ℃, defects in epitaxial graphene decreased and graphene has a perfect lattice.

In Refs. [16–20], Raman spectroscopy was performed to monitor the characteristics of epitaxial graphene on SiC substrate. A smaller $I_{\rm D}/I_{\rm G}$ and more than one of $I_{\rm 2D}/I_{\rm G}$ indicate that a larger size and few-layer graphene has grown on SiC substrates, which corresponds higher degree of graphitization process, where $I_{\rm D}$, $I_{\rm G}$, $I_{\rm 2D}$ are the intensities of D, G and 2D band respectively. As can be seen from Fig. 2, during the increase of temperatures from 1400 to 1600 ℃, $I_{\rm D}/I_{\rm G}$ becomes smaller and $I_{\rm 2D}/I_{\rm G}$ larger, which shows that there was few-layer graphene grown on substrates with larger size. Furthermore, $I_{\rm D}$ is weaker and weaker, which indicates that the defects and imperfect lattice degraded. So we suppose that if keeping increasing the growing temperature, 2D band will be sharper and stronger, D band will be weaker and weaker, which indicate that thinner few-layer even mono-layer graphene come into being on substrates with higher quality, this results are in good agreement with Ref. [21]. Due to the limitations of our growing device, it does not reach higher temperature above 1600 ℃, we could not grow epitaxial graphene samples at higher temperatures, but we come to a conclusion that raising growing temperature can improve the quality of graphene grown on substrates.

Figure 3 shows Raman spectroscopy in the frequency range from 600 to 3500 cm^{-1} of graphene sample grown at 1600 ℃. We can see that there are other bands except for D, G and 2D bands appeared. Bands of 788 cm^{-1} E$_2$(TO) and 965 cm^{-1} A$_1$(LO) are from 6H-SiC substrate[22], G* band (around 2453 cm^{-1}) comes from graphene, which corresponds to the combination of T and D$_2$ observed in the edges of FBZ[16, 23]. Weak 2D$'$ band (around 3245 cm^{-1}) is also a characteristic of graphene, it is the second order band of D$'$ band (around 1620 cm^{-1})[24]. The inset of Fig. 3 shows that 2D band can be fitted with a single-Lorentzian function with a full-width at half-maximum (FWHM) 60 cm^{-1}. Calculated

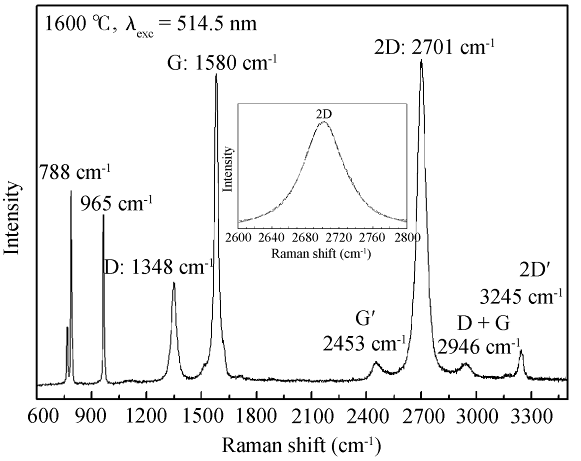

Fig. 3. Raman spectroscopy of epitaxial graphene on 6H-SiC ($000\bar{1}$) substrate at 1600 ℃ under a pressure of 2 mbar. Inset shows the 2D band can be fitted with a one-Lorentzian function, the shape and position reveal turbostratic graphite.

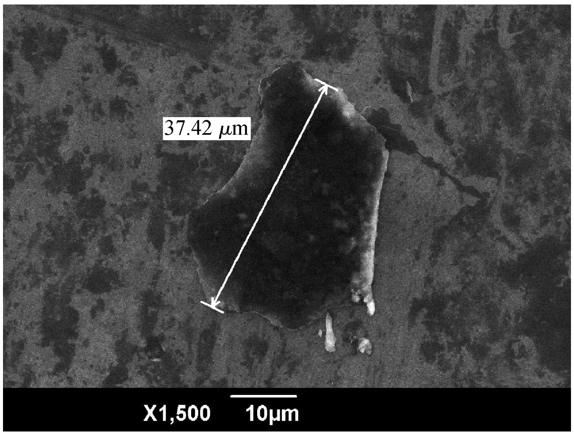

Fig. 4. Map of SEM of epitaxial graphene on 6H-SiC ($000\bar{1}$) substrate grown at 1600 ℃ under a pressure of 2 mbar environment.

FWHM(D) = 35 cm^{-1}, FWHM(G) = 25 cm^{-1}, we can judge that epitaxial graphene has a property of turbostratic multilayer graphite[25, 26].

Figure 4 further shows the map of SEM of turbostratic graphite sample grown at temperature 1600 ℃ under low pressure of 2 mbar condition. We observe that it has a size of 10 μm, which is much larger than that of graphene grown under UHV in Ref. [10]. The reason for this can be explained as follows: graphene grown on SiC substrate is a Si-sublimation followed with C self-organization process. Under UHV condition, Si atom has a over-quick sublimating rate, which holds back C rearranged hexagonal lattice; argon atmospheric environments has a over-large pressure for Si and Si is hard to sublimate from SiC substrate, so graphene can not grow larger size also. Appropriate pressure can adjust the rate of Si sublimation and C re-construction, graphene is easy to grow larger with higher quality.

4. Conclusions

In conclusion, this work investigated the growing characteristics of epitaxial graphene under low pressure of 2 mbar condition. Raman analysis shows that in comparison with epitaxial graphene grown under UHV and argon atomospheric pressure, a lower pressure environment is useful for growing larger size and higher quality graphene. Meanwhile, higher temperatures can help make and optimize the quality of graphene. We hope our research will provide a new method for making larger size even wafer scale graphene.

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