Raman analysis of epitaxial graphene grown on 4H–SiC (0001) substrate under low pressure condition*

Wang Dang-Chao(王党朝)[a)b)†], Zhang Yu-Ming(张玉明)[a)], Zhang Yi-Men(张义门)[a)], Lei Tian-Min(雷天民)[a)], Guo Hui(郭 辉)[a)], Wang Yue-Hu(王悦湖)[a)], Tang Xiao-Yan(汤晓燕)[a)], and Wang Hang(王 航)[a)]

[a)] *School of Microelectronics, Key Laboratory of Wide Band-Gap Semiconductor Materials and Devices, Xidian University, Xi'an* 710071, *China*

[b)] *School of Physics and Electronic Engineering, Xianyang Normal College, Xianyang* 712000, *China*

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In this paper, we report a feasible route of growing epitaxial graphene on 4H–SiC (0001) substrate in a low pressure of 4 mbar (1 bar=10^5 Pa) with an argon flux of 2 standard liters per minute at 1200, 1300, 1400, and 1500 °C in a commercial chemical vapour deposition SiC reactor. Using Raman spectroscopy and scanning electron microscopy, we confirm that epitaxial graphene evidently forms on SiC surface above 1300 °C with a size of several microns. By fitting the 2D band of Raman data with two-Lorentzian function, and comparing with the published reports, we conclude that epitaxial graphene grown at 1300 °C is four-layer graphene.

Keywords: SiC substrate, epitaxial graphene, Raman spectroscopy

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1. Introduction

Epitaxial graphene on SiC substrate has created the opportunity for graphene-based devices in the past few years.[1−11] There are many factors to affect the formation of epitaxial graphene and the different growth conditions will produce different morphology of epitaxial graphene. It is still questionable to make a large and uniform epitaxial graphene on SiC with low defect densities. Many experiments in this field have grown epitaxial graphene under the ultra-high vacuum (UHV) environment[9,12] or argon ambience under atmospheric pressure,[13] and there were few reports for growing graphene under lower pressure condition. References [14] and [15] suggested that the formation of epitaxial graphene does not require an UHV environment. In this work, epitaxial graphene films grown on 4H–SiC (0001) (Si-face) substrate were demonstrated under low pressure of 4 mbar (1 bar=10^5 Pa) at temperatures from 1200 °C to 1500 °C and Raman scattering technique has been used to analyse the formation of epitaxial graphene.

2. Experiment

Epitaxial graphene was grown on the 4H–SiC (0001) substrate with 0° cut-off the c axis, high-resistivity and n-type nitrogen concentration about 10^{15} cm^{-3}. The substrate was cut into 2 cm×1 cm pieces and then pre-cleaned to removing the surface contaminants before entering in the chamber of the Epigress VP508 SiC Hot-Wall Chemical Vapour Deposition (CVD) reactor. The process of epitaxial graphene growth consists of two steps, i.e. hydrogen etching and epitaxial growth. It is necessary to carry out for polishing the damage of the substrate surface with a flux of hydrogen at 1600 °C. In the following, growth process was implemented with argon flux of 2 standard liters per minute under the pressure of 4 mbar at temperatures from 1200 °C to 1500 °C. Using an alternating current (AC) mode atomic force microscopy (AFM: Agilent 5500), we have observed a regularly stepped surface with a root-mean-square roughness of the height 2.78 nm on the SiC (0001) substrate, as shown in Fig. 1.

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†Corresponding author. E-mail: wangdangchao@yahoo.com.cn

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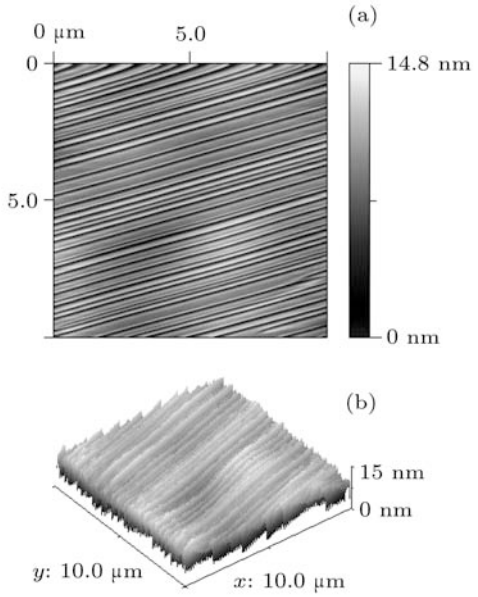


Fig. 1. Typical AFM height images: (a) two-dimensional image; (b) three-dimensional on 4H–SiC (0001) substrate after hydrogen etching of the same zone in 10 μm×10 μm.

Scanning electron microscopy (SEM: JEOL JSM-6390A) is used to observe the size of epitaxial graphene on SiC substrate. Raman data were collected from the micro-Raman Spectrometer (Renishaw inVia Raman microscope) at room temperature, excited by the 514.5 nm (2.41 eV) visible laser beam from He–Cd laser. To avoid local surface damage by laser-induced heating, the power injected on top of the samples is as low as 2 mW or below.

3. Results and discussion

It is widely accepted that Raman spectroscopy can provide a fast and non-destructive technique for differentiating between different carbon phases in the process of growing epitaxial graphene on SiC substrate. Raman spectroscopy of epitaxial graphene shows two prominent characteristics: the G band and the 2D band. The G band (graphite-like mode) originates from the first order (one phonon) Raman scattering process, and it is the characteristic of sp^2 hybridization and involves the in-plane optical phonon E_{2g} near the first Brillouin zone centre (Γ point) of the phonon band structure.[16] The 2D band is a second-order band due to two phonons with opposite momentum in the highest optical branch near the Dirac point K (K').[16] The disorder-induced D band often clearly appears in Raman spectroscopy, which is sensitive to domain size, the disorder and edges defects in the lattice structures.[9]

Raman spectroscopy of epitaixal graphene on 4H–SiC (0001) substrate is shown in Fig. 2. It can be seen from this figure that the G band is positioned around 1582 cm^{-1}. Also because there is SiC remaining on the epitaxial graphene, the G band is nearly invisible in Raman spectroscopy from 1450 cm^{-1} to 1750 cm^{-1} in (d) and (e).[17,18] Moreover, the D band appears near 1354 cm^{-1}, indicating that there are defects in our samples. The 2D band shown in Fig. 2(c) is about 2704 cm^{-1}, while in Figs. 2(d) and 2(e) is 2722 cm^{-1}, which is a result of the strain which comes from lattice mismatches in the interface between the underlying substrate and epitaxial graphene, giving the 2D band in Raman spectroscopy a different shape and position when the growing temperature rises, leading to the up-shifted 2D band frequency. Figure 3 shows the 2D band of Raman spectroscopy in the frequency range from 2600 cm^{-1} to 2800 cm^{-1} of epitaxial graphene in detail at different growing temperatures.

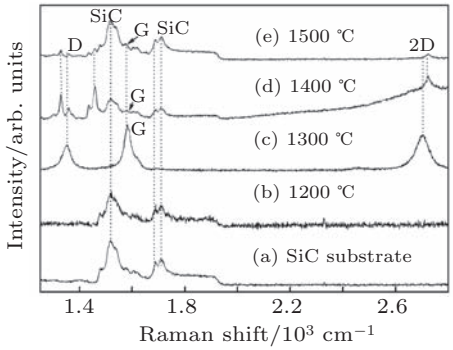


Fig. 2. Raman spectroscopy at excitation wavelength 514.5 nm for epitaxial graphene under low pressure of 4 mbar at different temperatures. From (b) to (e), the temperature increases from 1200 °C to 1500 °C. The Raman raw data are normalized.

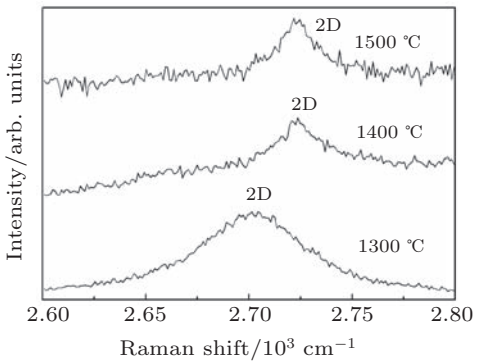


Fig. 3. The map of the 2D band of Raman spectroscopy of epitaxial graphene on 4H–SiC (0001) substrate grown at 1300 °C, 1400 °C, and 1500 °C, under a pressure of 4 mbar.

From the Raman results, it can be found that the quality of epitaxial graphene above 1300 °C is not as good as we initially expected, and the reason needs

to be investigated in depth. Although exhibiting different band positions, we find that epitaxial graphene layers are continuous in sizes with the order of magnitude of microns as shown in Fig. 4.

It is found that the bandwidth of the 2D band of Raman spectroscopy is an unambiguous fingerprint which distinguishes the layer number of epitaxial graphene on SiC (0001),[19] so figure 5 can be used to estimate the layer number of epitaxial graphene. It can be seen from this figure that at a temperature of 1300 °C the 2D band near 2704 cm^{-1} has a single sharp and symmetric peak, which marks that graphene is indeed grown on the substrate. The G band has a more intense signal than that of the 2D band, which corresponds to a thicker graphene film. The 2D band has a full width at half maximum (FWHM) of 60 cm^{-1}, and can be fitted with a two-Lorentzian function as shown in the inset of Fig. 5, and the G band near 1582 cm^{-1} with an FWHM of 32 cm^{-1}, which is well in line with four-layer graphene on SiC (0001) in Ref. [16], so we conclude that four-layer epitaxial graphene has grown on SiC substrate at 1300 °C.

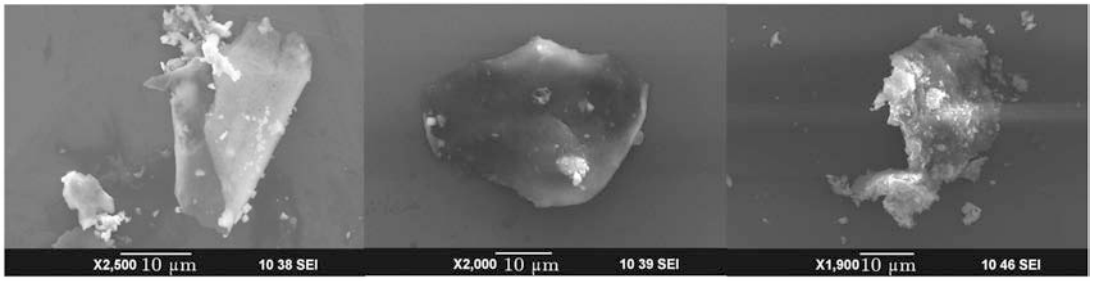


Fig. 4. The SEM map of epitaxial graphene on 4H–SiC (0001) substrate grown at (a) 1300 °C, (b) 1400 °C, and (c) 1500 °C under a pressure of 4 mbar.

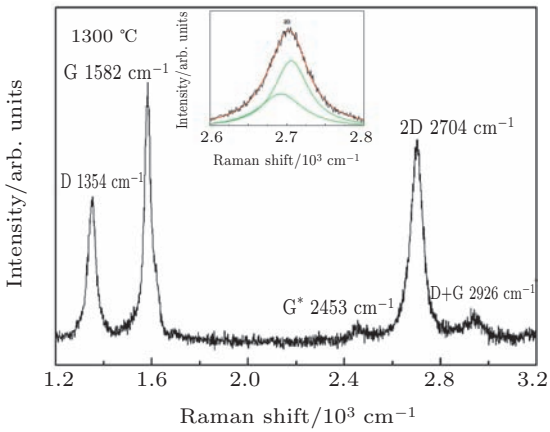


Fig. 5. (colour online) Raman spectroscopy of epitaxial graphene grown on 4H–SiC (0001) substrate at temperature of 1300 °C under a pressure of 4 mbar. Inset shows that the 2D band can be fitted with a two-Lorentzian function, the shape and position reveal four-layer graphene.

4. Summary

In summary, epitaxial graphene has been grown on 4H–SiC (0001) substrate in a low pressure condition at different temperatures from 1200 °C to 1500 °C. Raman spectroscopy analysis of these processes reveals that there is no evidence of graphene grown at temperature below 1200 °C, the formation of epitaxial graphene requires at least 1300 °C with a size of several microns, and by comparing the characteristic of Raman spectroscopy with the reported results in details, we make a reasonable estimation that epitaxial graphene grown at 1300 °C is four-layer in thickness. This work will be helpful for further study on epitaxial graphene.

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