Structural Strain in Single Layer Graphene Fabricated on SiC

Wancheng Yu^{1,2,3}, Xiufang Chen^{1,*}, Xiaobo Hu¹, Xiangang Xu¹, Peng Jin^{2,3}, Peng Yu⁴ and Ruiqi Wang⁴

¹State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, P. R. China

²Key Laboratory of Semiconductor Materials Science and Beijing Key Laboratory of Low-Dimensional Semiconductor Materials and Devices, Institute of Semiconductors, Chinese Academy of Science, Beijing 100083, P. R. China

³College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing, 101408, P. R. China

⁴Collaborative Innovation Center for Global Energy Interconnection (Shandong), Jinan, 250061, P. R. China

*cxf@sdu.edu.cn

Keywords: Graphene, SiC, KPFM, Strain

Abstract. Single layer graphene was fabricated on the Si face of silicon carbide through thermal decomposition. The thickness of graphene was checked by a combination of *ex situ* Kelvin probe force microscopy together with Raman spectroscopy and atomic force microscopy. The amount of residual strain induced was calculated to between 1.3% and 0.7%. Results also show that the magnitude of strain increased with growth time while the uniformity of strain improved.

Introduction

Graphene is a two dimensional carbon allotrope with carbon atoms being sp^2 hybridized and densely packed into a hexagonal honeycomb lattice. It has attracted much attention as one of the most promising material in microelectronic field. For graphene grown on semi-insulating SiC substrates, devices can be fabricated directly without additional transfer to another insulator. Therefore, fabrication of graphene through thermal decomposition on SiC has been extensively investigated [1].Growth of epitaxial graphene on SiC (0001) (Si face) is of particular interest as it is relatively easier to control the thickness of graphene on Si face [2].

In the previous studies, atomic force microscopy (AFM) and scanning electron microscope (SEM) were widely used to confirm the thickness of graphene [3]. However, due to the step morphology of SiC substrate, determination of graphene thickness by standard AFM characterization is infeasible. On the other hand, though sectional SEM images could provide direct number of graphene layers, the morphology of graphene in horizontal direction is lacking. In this paper, a convenient way to characterize the grown surface is provided by Kelvin probe force microscopy (KPFM). KPFM is a noncontact variant of AFM coupled with electrostatic force measurements. The obtained surface potential mapping was used to study nanoscale variations of graphene.

In contrast to exfoliated graphene films, the nature of epitaxial graphene is effected remarkably by the interaction with substrate. Graphene has a negative thermal expansion coefficient between the growth temperature and room temperature while SiC holds a positive one. Therefore, large compressive strain exists in graphene fabricated on SiC. To apply graphene to electronic devices, the distortion of graphene should be explored thoroughly. Ferralis et al. [4] investigated the magnitude of the compressive strain by adjusting the growth time at fixed annealing temperature. However, the thickness of graphene, which will also influence the residual strain, changes with varied growth time. In this paper, single layer graphene was grown and compared to investigate the residual stress. Graphene samples were grown at different growth time with thickness confirmed by Raman spectroscopy and KPFM.

Experimental Procedure

Epitaxial graphene was prepared in a home-made conventional physical vapor transport growth system [5]. During the growth, a graphite enclosure was employed to provide the essential confinement for silicon sublimation. The substrates were nominally on-axis semi-insulting 4H-SiC wafers grown by Shandong University which were chemomechanically polished on the Si face. Before graphitization, an etching by hydrogen at 1600 °C took place to remove subsurface damage. Graphene was then grown under Argon atmosphere of 800 mbar. Single layer graphene films were systhisized after 10 min at 1620 °C, 30 min at 1610 °C and 50 min at 1600 °C, separately.

A JobinYvon-Horiba HR800 spectrometer was used to obtain micro-Raman spectroscopy. The as-prepared graphene surface was characterized by AFM and KPFM through a Dimension Icon scanning probe microscope of Veeco Instruments.

Results and Discussion

In this paper, KPFM associated with Raman spectroscopy was utilized to characterize the thickness of graphene. To demonstrate the accuracy of this measurement, graphene samples of different thickness were fabricated through varied growth time from 10 min to 50 min at a fixed growth temperature of 1650 °C. Substrates with only hydrogen etching were also measured for comparison, referred as 0 min growth.

Typical Raman maps of 2D band intensity are shown in Figure 1, Figure 1(a)-(d) represent substrates after 0 min, 10 min, 30 min and 50 min growth respectively. During the hydrogen etching, no graphene was formed. After 10 min anneal under argon, it can be observed that area with graphene characteristic peak began to emerge. With a prolonged growth time of 30min, graphene spreaded out to most of the surface. For substrates after 50 min growth, graphene has covered the whole surface.



Figure 1 Raman image plotted by intensity of the 2D band for graphene fabricated at (a) 0min (b)10min (c)30min (d)50min and (e)the interpretation of Raman spectra

Note that the first carbon layer grown on the Si face of SiC is known as buffer layer which has strong covalent bonds with substrate. Thus, the buffer layer exists neither graphitic electronic properties nor typical graphene Raman figures. The next carbon layer on buffer layer starts to behave electronically like an isolated graphene sheet and is therefore regarded as the first graphene layer. The buffer layer can be identified by broad features between 1200 and 1665 cm⁻¹ [6]. Results showed that buffer layer existed in the dark area of Fig1 (b) and (c), the Raman sepctrum of buffer layer and the interpretation of graphene are shown in Fig 1 (e).

By utilizing Raman mapping, graphene can be clearly distinguished. However, Raman studies of multilayered graphene were conducted by comparing the intensity ratio, shape or linewidth of 2D peak, which is relatively complicated [7]. In this paper, KPFM was utilized to characterize the thickness of graphene on same samples, results are shown in Figure 2. Figure 2 (a)-(d) are the morphology of substrates after 0 min, 10 min, 30 min and 50 min growth measured by AFM, Figure 2 (e)-(h) are the corresponding potential map measured by KPFM. For substrate with only hydrogen etching, the surface potential remained a constant across all region, demonstrating that the step morphology of substrate has no effect on surface potential. After 10 min growth, area with higher surface potential appeared at the step edge. Compare with the distribution of Raman spectrum, it can be inferred that the higher potential area correspond to graphene. In a similar way, we can determine that, after 30 min growth graphene spreaded out from step edge to the terrace. For samples after 50 min growth, higher potential area appeared at the step edge again. As Raman spectrum had proven that the whole surface covered by graphene, we suppose that the higher potential area has a thicker graphene layer. With the combination of KPFM and Raman spectroscopy, growth trend and thickness of graphene can be clearly distinguished.



Figure 2 KPFM potential distribution image (upper layer) and corresponding AFM morphology (lower layer) for graphene fabricated at (a) (e) 0min (b) (f)10min (c) (g)30min and (d) (h)50min

Structural strain of graphene was investigated by the peak shift of Raman spectrum. G peak is often chosen in investigation of exfoliated graphene. However, the second order Raman signal of SiC overlaps with the G peak of Raman spectrum. On the other hand, the 2D peak of graphene is not affected by characteristic peaks of SiC. Besides, peak position of 2D peak changes little by electron density when it is less than 3.2×10^{13} cm⁻² [8]. In our samples, the electron density was around 1×10^{13} cm⁻². Therefore, 2D peak was chosen instead of G peak to characterize the residual strain. The relationship between 2D peak shift $\Delta\omega$ and compressive strain ϵ is given by

$$\Delta\omega/\omega = -\gamma_{2D}tr\epsilon,\tag{1}$$

where γ_{2D} is the mode Gruneisen parameter. Raman peak shift of 2D band with varied growth time is shown in Figure 3. All data were derived from single layer graphene confirmed by KPFM and Raman spectroscopy. The samples were obtained at different growth time by varying temperature. For samples after 10 min, 30 min and 50 min growth, the growth temperature was 1620 °C, 1610 °C and 1600 °C under Argon atmosphere of 800 mbar. Results show that the compressive strain increased with the increasing growth time. The value of strain can be varied from 0.7% to 1.3%.

The strain induced by temperature can be calculated by

$$1/(1-\epsilon) = exp\left[\int_{RT}^{T_s} dT \Delta \alpha(T)\right],\tag{2}$$

where RT is room temperature, T_s is the growth temperature, $\Delta \alpha(T)$ is the difference in thermal expansion coefficient between graphene and SiC. According to this formula, the strain will increase with higher growing temperature. However, the strain was decreased in our samples with high growing temperature and less growing time, indicating that the increase of strain was caused by growth time. Although a short annealing time could decrease the strain, the uniformity of strain across the sample deteriorated. Only after long annealing time mechanical equilibrium between epitaxial graphene and substrate can be achieved. To obtain high quality graphene layer, both the magnitude and the homogeneity of strain should be taken into consider.



Figure 3 Raman 2D peak position for graphene fabricated at different annealing time

Summary

In summary, single layer graphene was confirmed by a combination of Raman and KPFM. Besides, Raman spectroscopy was used to assess the strains in graphene samples. For graphene fabricated under annealing time between 10 minutes to 50 minutes, the strain varied between 1.3% and 0.7%.

Acknowledgment

This work has been funded by the National Key Research and Development Program of China (Grant No. 2018YFB0406501 & 2018YFB0406703), the Beijing Municipal Science and Technology Commission (Grant No. Z181100004418009), the National Natural Science Foundation of China (Grant No. 51702313), Province Key R&D Program of Shandong (Grant No. 2016GGX4101), Fundamental Research Funds for Natural Science of Shandong University (Grant No. 2016JC037), Science and Technology Project of State Grid Corporation of China (SGSDDK00KJJS1600063, SGSDDK00KJJS1600071) and Foundation 31513020404-1.

References

[1] K. V. Emtsev, A. Bostwick, K. Horn, et al. Towards Wafer-size Graphene Layers by Atmospheric Pressure Graphitization of Silicon Carbide, Nat. Mater. 8.3 (2009) 203-207.

[2] I. Forbeaux, J. M. Themlin, A. Charrier, et al. Solid-state graphitization mechanisms of silicon carbide 6H–SiC polar faces, Appl. Surf. Sci. 162 (2000) 406-412.

[3] C. Dimitrakopoulos, Y. M. Lin, A. Grill, et al. Wafer-scale epitaxial graphene growth on the Siface of hexagonal SiC (0001) for high frequency transistors, J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct. 28.5 (2010) 985-992. [4] N. Ferralis, R. Maboudian, C. Carraro. Evidence of structural strain in epitaxial graphene layers on 6H-SiC (0001), Phys. Rev. Lett. 101.15 (2008) 156801.

[5] X. Hu, X. Xu, X. Li, et al. Stacking faults in SiC crystal grown by spontaneous nucleation sublimation method, J. Cryst. Growth 292.2 (2006) 192-196.

[6] F. Fromm, Jr MHO, A. Molinasánchez, et al. Contribution of the buffer layer to the Raman spectrum of epitaxial graphene on SiC(0001), New J. Phys. 15.16 (2014) 043031.

[7] J. S. Park, A. Reina, R. Saito, et al. Band Raman spectra of single, double and triple layer graphene. Carbon 47.5 (2009) 1303-1310.

[8] A. Das, S. Pisana, B. Chakraborty, et al. Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor, Nat. Nanotechnol. 3.4 (2008) 210-215.