Graphene films grown on sapphire substrates via solid source molecular beam epitaxy*

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A method for growing graphene on a sapphire substrate by depositing an SiC buffer layer and then annealing at high temperature in solid source molecular beam epitaxy (SSMBE) equipment was presented. The structural and electronic properties of the samples were characterized by reflection high energy diffraction (RHEED), X-ray diffraction Φ scans, Raman spectroscopy, and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The results of the RHEED and Φ scan, as well as the Raman spectra, showed that an epitaxial hexagonal α-SiC layer was grown on the sapphire substrate. The results of the Raman and NEXAFS spectra revealed that the graphene films with the *AB* Bernal stacking structure were formed on the sapphire substrate after annealing. The layer number of the graphene was between four and five, and the thickness of the unreacted SiC layer was about 1–1.5 nm.

Keywords: graphene, SiC layer, sapphire substrate

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1. Introduction

Graphene is a recently discovered material which consists of a single layer of sp^2-bonded carbon atoms arranged in a two-dimensional honeycomb lattice. Due to its unique electronic and optical properties, such as massless Dirac fermion, exceedingly high carrier mobility, and ballistic transport at room temperature, graphene has attracted much attention as a potential material for next generation electronic devices.[1−4] Moreover, some remarkable properties are also possessed by bilayer and few-layer graphene.[3−5] Since the discovery of isolated graphene through mechanical exfoliation of highly oriented pyrolytic graphite (HOPG),[4] a number of other methods have been explored to produce this material, which include reduction of graphene oxide,[6,7] chemical vapor deposition of hydrocarbons,[8,9] splitting carbon nanotubes to form graphene ribbons,[10] and ultrahigh vacuum (UHV) annealing of SiC wafers.[11,12] Whereas the UHV annealing of single crystal hexagonal SiC has been demonstrated to be one of the most reliable ways to produce high quality graphene films.[11] However, commercial SiC wafers remain limited in size and high in price, so other substrates should be considered for the growth of graphene. In our previous work, we grew graphene films on Si (111) substrates by direct precipitating solid-state carbon atoms.[13] Sapphire is also likely to be a fine substrate for growing graphene.[14] Recently, some attempts to grow graphene layers on a sapphire substrate were reported.[15−17] Ago *et al.*[15] and Ismach *et al.*[16] tried to obtain graphene with the help of the surface catalytic decomposition of hydrocarbons. While Timothy *et al.*[17] firstly grew polycrystalline SiC and then annealed it in vacuum to create epitaxial multilayer graphene. However, all these methods employed chemical vapor deposition (CVD). Molecular beam epitaxy (MBE) is a well known and widely used technique for the production of high quality and homogeneous wafer-scale epitaxial layers. It is highly reproducible with atomic layer control of thickness

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and composition. These advantages make MBE an attractive growth method for graphene films. However, there have only been a few experimental attempts to grow graphene by MBE.[18,19] In this paper, we present a method by depositing an SiC buffer layer on a sapphire substrate and then annealing it at high temperature in the MBE equipment. The α-type SiC thin films are grown by solid source molecular beam epitaxy (SSMBE). As the common thermodynamical stability is broken in the SSMBE case, the formation temperature of SiC thin films grown by SSMBE is much lower than that of SiC thin films grown by CVD.[20−22]

2. Experiment

The samples were prepared in an MBE system equipped with an RHEED instrument. The base pressure was 6.0×10^{-8} Pa. Si and C sources with a purity of 99.999% were both supplied by e-beam evaporators.[23] The deposition rates of Si and C were measured by quartz crystal oscillators (MAXTEKTM-350) with a precision of 0.1 nm. The sapphire substrates were dipped into acetone and cleaned with an ultrasonic washer for 5 min, and then rinsed several times with deionizer water. After being dried in a flux of N_2, the substrates were immediately placed into the chamber. Two samples were prepared. For sample 1 (S1), an SiC thin film with a thickness of 5 nm was grown on a *c*-plane sapphire wafer at 1100 °C by co-deposition of Si and C atoms. The deposition rates of the Si and C atoms were 0.5 nm·min^{-1} and 0.3 nm·min^{-1}, respectively. For sample 2 (S2), an SiC thin film was first grown on the sapphire substrate under the same conditions as S1, and then annealed *in situ* at 1350 °C for 5 min. Finally, the samples were cooled down to room temperature over 60 min.

During the preparation process, the sample surface was monitored *in situ* by RHEED, which was operated at an accelerating voltage of 21 kV and an ejecting current of 50 μA. Raman spectra were taken using an Ar-ion laser with a wavelength of 514.5 nm. C *K*-edge NEXAFS and X-ray diffraction Φ scan measurements were performed on beam lines U7B and U19 of the National Synchrotron Radiation Laboratory (China), respectively.

3. Results and discussion

As shown in Fig. 1, a series of RHEED patterns were taken along the [1$\bar{1}$00] during the preparation process of sample 2. Figure 1(a) shows the diffraction fringes and the kikuchi lines of the sapphire wafer, which indicate that the substrate surface is clean. When Si and C atoms are co-deposited on the substrate at 1100 °C for a few minutes, the diffraction fringes of the sapphire disappear gradually. Meanwhile, the diffraction streaks of SiC appear along [1$\bar{1}$00] (Fig. 1(b)), which denotes that an SiC layer is grown on the sapphire substrate. According to our previous results for SiC thin films grown on the sapphire substrate, we can see the peaks of SiC (0006) and Al_2O_3 (0001) in the same XRD pattern, indicating that the SiC thin films and the sapphire substrate should be of the same orientation.[24] After annealing at 1350 °C, the diffraction streaks of the SiC film become obscure, as shown in Fig. 1(c). However, a new diffraction streak is found between two SiC diffraction streaks along [1$\bar{1}$00]. Similarly, Kulber *et al.*[25] observed very clear diffraction streaks of the graphene film that appeared beside the SiC diffraction streaks along [1$\bar{1}$00] after annealing 6H-SiC (0001) at high temperature. Therefore, the appearance of the new diffraction streak might reveal the formation of the graphene film on the surface of sample 2. As the growth conditions of the SiC layer of sample 1 are the same as those of sample 2, the SiC layers of samples 1 and 2 should have similar structural properties.

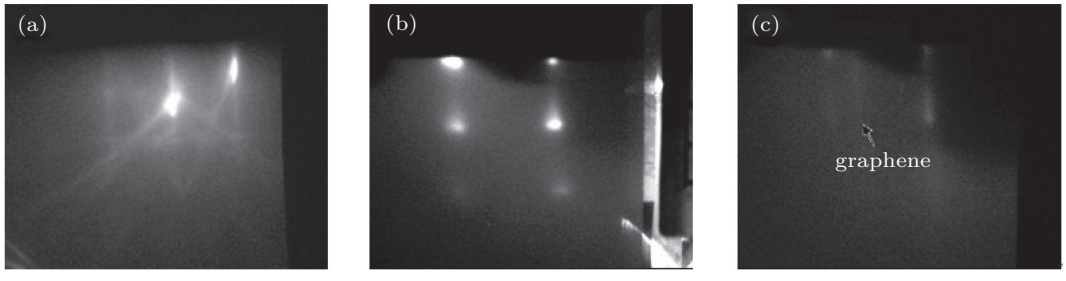


Fig. 1. RHEED patterns acquired along the [1$\bar{1}$00] azimuth of sample 2: (a) sapphire substrate, (b) SiC film grown on sapphire at 1100 °C, (c) sample annealed at 1350 °C.

In order to check the quality of the SiC layer and distinguish the polytype, we carried out an X-ray diffraction Φ scan measurement of sample 1 with a wavelength of 1.25 nm.[26] Figure 2 shows the pattern when the grazing incidence angle is fixed at 0.25° and the reflection selected for the Φ scan is along $[11\bar{2}0]$. After the Φ angle is scanned 360°, sixfold symmetrical diffraction peaks of the SiC layer appear. There are six sixfold symmetrical diffraction peaks, and the angle between any two adjacent peaks is 60°, which indicates that the epitaxial SiC layer has better crystalline quality. Combined with the following Raman results, we can also ascertain that the epitaxial SiC layer should belong to the α-SiC polytype.

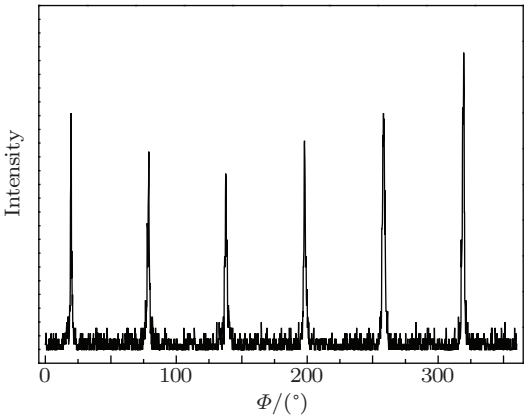


Fig. 2. X-ray diffraction Φ scan of sample 1.

Raman spectroscopy has been extensively utilized as a convenient technique for identifying graphene.[27] Figure 3(a) shows the Raman spectra of samples 1, 2 and HOPG. As shown in the Raman spectrum of sample 1, there are three bands located at 420 cm^{-1}, 765 cm^{-1}, and 965 cm^{-1}, respectively. The band located at 420 cm^{-1} comes from the sapphire substrate, and the two bands located at 765 cm^{-1} and 965 cm^{-1} correspond to the transverse optical (TO) and the longitudinal optical (LO) phonon modes of SiC.[28] The TO phonon mode exhibits a pronounced splitting structure, and the intensity of the TO phonon mode is much stronger than that of the LO phonon mode, indicating that the epitaxial SiC layer has a hexagonal lattice structure and should belong to the α-SiC polytype.[28] As for the Raman spectrum of sample 2, besides the peaks of sapphire and SiC, there are three sharp bands located at 1361 cm^{-1}, 1592 cm^{-1}, and 2735 cm^{-1}, which correspond to the D, G, and 2D modes in the Raman spectrum of graphene, respectively.[27] Generally, the G band is due to a one phonon process involving Γ-point optical phonons, and is the characteristic of the sp^2-bonded carbon, while the 2D band results from a two-phonon resonant scattering process.[2] The presence of the 2D band can indicate the electronic structure dominated by the Dirac–Weyl dispersion and is used as the typical signature for the presence of graphene.[27,29] The appearance of the G and 2D modes in the Raman spectrum of sample 2 indicates that the graphene layers are formed on the sapphire substrate after annealing. The so-called disorder-induced D mode can also be observed, which implies that the graphene films contain some defects. Moreover, the band located at 420 cm^{-1} comes from the sapphire substrate, and the two bands located at 765 cm^{-1} and 965 cm^{-1} correspond to SiC, which show that the SiC layer does not completely decompose after annealing. Generally, the layer number and the stacking structure of the graphene can be reflected by the G and 2D bands of the Raman spectra.[27,29,30] There are two stacking structures of the graphene layers, which are *AB* Bernal stacking and turbostratic stacking.[30] The graphene layers with an *AB* Bernal stacking structure, in which the in-plane orientation of the graphene layers is single, are mainly prepared by the mechanical exfoliation of HOPG and the thermal annealing of the Si-terminated α-SiC wafer. The graphene layers with a turbostratic stacking structure, in which the in-plane orientations of the graphene layers are different, are typically prepared by thermal annealing the C-terminated α-SiC. It is noted that the identification of the different graphene stacking structures can utilize the position and the shape of the 2D mode of the Raman spectrum. For the single graphene layer with an *AB* stacking structure, the 2D mode is only composed of a single Lorentzian component, while for a more than one layer film, it is composed of several Lorentzian components.[30] For the turbostratic graphene, no matter how many layers there are, the Raman 2D mode is composed of a single Lorentzian component, just like the monolayer graphene but with a larger linewidth. In order to identify the graphene stacking structure of sample 2, the 2D mode of sample 2 was fitted. Figure 3(b) shows the line shape fits of the 2D bands for the HOPG and sample 2. As shown in Fig. 3(b), the 2D mode of sample 2 is not asymmetric and is fitted into two peaks located at 2696 cm^{-1} and 2741 cm^{-1}, respectively. Compared to the two fitted peaks of the 2D mode in the HOPG located at 2684 cm^{-1} and 2726 cm^{-1}, there are shifts of 12 cm^{-1} and 15 cm^{-1} in the 2D Raman peaks of sample 2, respectively. Analogously, the shift of the 2D mode in sample 2 towards high frequency agrees with that of the few-layer graphene on the Si-terminated 6H-

SiC.[31,32] Thus, it can be inferred that the graphene films have formed on the surface of sample 2 with an *AB* Bernal stacking structure, just like the few-layer graphene grown on the Si-terminated 6H-SiC. It was reported that for the few-layer graphene grown on the Si-terminated 6H-SiC, the interface interaction between the graphene and the 6H-SiC substrate was strong, and that interface states existed.[33] As the graphene layer grown with our method has a similar stacking structure to that of the few-layer graphene grown on the Si-terminated 6H-SiC, we can deduce that the interface interaction between the graphene layer and the unreacted SiC might have a similar strong interface interaction. The intensity ratio of the G band to the $2D$ band, I_{2D}/I_G, is normally used for identifying the number of atomic graphene layers from $n = 1$ to approximately $n = 19$.[34] We calculated the value of I_{2D}/I_G ($I_{2D}/I_G = 1.13$) and deduced that the layer number of the graphene is between four and five by referring to the results of Gupta *et al.*[34] As one graphene layer requires the decomposition of 3.14 SiC bilayers, the thickness of the unreacted SiC layer is about 1–1.5 nm.

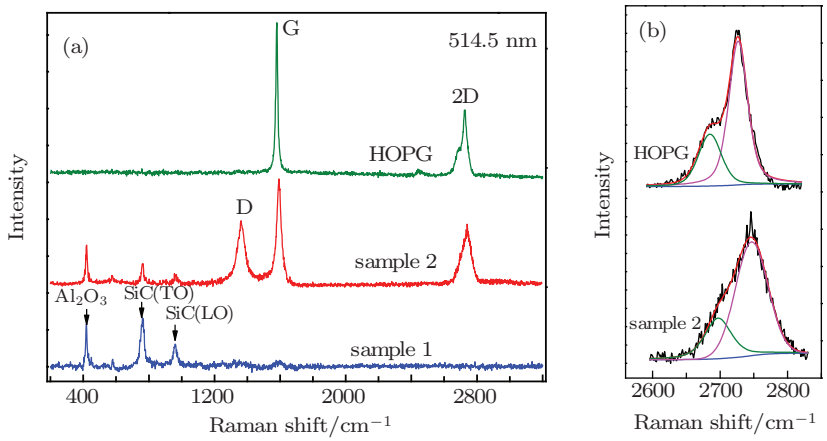


Fig. 3. (colour online) (a) Raman spectra of samples 1, 2 and HOPG, (b) line shape fits of the 2D bands of HOPG and sample 2.

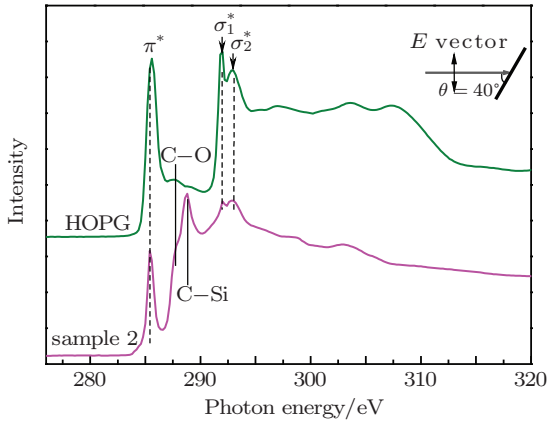


Fig. 4. (colour online) C K-edge NEXAFS spectra of HOPG and sample 2.

NEXAFS is a powerful tool for studying the electronic and atomic structures of a material. In order to confirm the formation of graphene, we carried out NEXAFS measurements. Figure 4 shows the C K-edge absorption spectra of HOPG and sample 2. As shown in Fig. 4, there are mainly a π^* resonance peak located at around 285.5 eV and a σ^* resonance peak located at around 292.4 eV in both spectra. Generally, the NEXAFS spectrum for graphite is well characterized by sharp 1s$\rightarrow \pi^*$ and 1s$\rightarrow \sigma^*$ peaks. Because the unit cell of the graphene contains two kinds of carbon atoms,[30] the σ^* peak in the C K-edge NEXAFS spectrum of the graphene is often split into two components, σ_1^* and σ_2^*. The existence of the π^* and split σ^* peaks are the fingerprints of the sp^2 hybridized C atoms in the hexagon network structure.[35] Therefore, the appearance of the π^* resonance peak and the σ_1^*, σ_2^* resonance peaks in the NEXAFS spectrum of sample 2 indicates that well-order sp^2 hybridized C atoms with a hexagon network structure exist. In addition, a peak at 287.1 eV exists in both absorption spectra shown in Fig. 4, which comes from the C=O π^* state due to surface oxidation.[36] Moreover, there is another peak located at 287.6 eV in the spectrum of sample 2, which comes from the C–Si sp^3 hybridization state of SiC.[36] Therefore, the NEXAFS results verify that the graphene films are formed after annealing the SiC buffer layer, and the SiC layer does not decompose completely, which is consistent with the Raman spectra results.

4. Conclusion

Graphene films were successfully fabricated on a sapphire substrate primarily through depositing an SiC buffer layer and then annealing at 1350 °C. The results of the RHEED and X-ray diffraction Φ scans, as well as the Raman spectra, showed that a well-ordered hexagonal α-SiC layer was grown on the sapphire substrate. The results of the Raman and NEXAFS spectra revealed that the graphene films with an *AB* Bernal stacking structure were formed after annealing the sample at high temperature. The layer number of the graphene was between four and five, and the thickness of the unreacted SiC layer was about 1–1.5 nm

References

[1] Novoselov K S, Jiang Z, Zhang Y, Morozov S V, Stormer H L, Zeitler U, Maan J C, Boebinger G S, Kim P and Geim A K 2007 *Science* **315** 1379

[2] Geim A K and Novoselov K S 2007 *Nature Mater.* **6** 183

[3] Li D and Kaner R B 2008 *Science* **320** 1170

[4] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666

[5] Novoselov K S, McCann E, Morozov S V, Falko V I, Zeitler U, Jiang D, Schedin F and Geim A K 2006 *Nature Phys.* **2** 177

[6] Su Q, Pang S, Alijani V, Li C, Feng X and Mullen K 2009 *Adv. Mater.* **21** 3191

[7] Ji Z Y, Wu J L, Shen X P, Zhou H and Xi H T 2011 *J. Mater. Sci.* **46** 1190

[8] Liu Z F, Liu Q, Huang Y, Ma Y F, Yin S G, Zhang X Y, Sun W and Chen Y S 2008 *Adv. Mater.* **20** 3924

[9] Lin T Q, Huang F Q, Liang J and Wang Y X 2011 *Energy & Environmental Science* **4** 862

[10] Kosynkin D V, Higginbotham A L, Sinitskii A, Lomeda J R, Dimiev A, Price B K and Tour J M 2009 *Nature* **458** 872

[11] Tang C J, Li J, Meng L J, Sun L Z, Zhang K W and Zhong K W 2009 *Acta Phys. Sin.* **58** 7815 (in Chinese)

[12] Kang C Y, Tang J, Li L M, Pan H B, Yan W S, Xu P S, Wei S Q, Chen X F and Xu X G 2011 *Acta Phys. Sin.* **60** 047302 (in Chinese)

[13] Tang J, Kang C Y, Li L M, Yan W S, Wei S Q and Xu P S 2011 *Physica* E **43** 1415

[14] Tsukamoto T and Ogino T 2009 *Applied Physics Express* **2** 075502

[15] Ago H, Ito Y, Mizuta N, Yoshida K, Hu B, Orofeo C M, Tsuji M, Ikeda K and Mizuno S 2010 *ACS Nano.* **4** 7407

[16] Ismach A, Druzgalski C, Penwell S, Schwartzberg A, Zheng M, Javey A, Bokor J and Zhang Y G 2010 *Nano. Lett.* **10** 1542

[17] McArdle T J, Chu J O, Zhu Y, Liu Z H, Krishnan M, Breslin C M, Dimitrakopoulos C, Wisnieff R and Grill A 2011 *Appl. Phys. Lett.* **98** 132108

[18] Park J, Mitchel W C, Grazulis L, Smith H E, Eyink K G, Boeckl J J, Tomich D H, Pacley S D and Hoelscher J E 2010 *Adv. Mater.* **22** 4140

[19] Hackley J, Ali D, DiPasquale J, Demaree J D and Richardson C J K 2009 *Appl. Phys. Lett.* **95** 133114

[20] Cimalla V, Stauden Th, Ecke G, Scharmann F, Eichhorn G, Cimalla V and Stauden Th 1998 *Appl. Phys. Lett.* **73** 3542

[21] Zekentes K, Papaioannou V and Pecz B 1995 *J. Cryst. Growth* **157** 392

[22] Li J C, Batoni P and Tsu R 2010 *Thin Solid Films* **518** 1658

[23] Wang K F, Liu J F, Zou C W, Xu P S, Pan H B, Zhang X G and Wang W G 2005 *J. Vac. Sci. Tech.* **25** 75

[24] Kang C Y, Liu Z L, Tang J, Chen X C, Xu P S and Pan G Q 2010 *Journal of Synthetic Crystals* **39** 308 (in Chinese)

[25] Kubler L, Aït-Mansour K, Diani M, Dentel D, Bischoff J L and Derivaz M 2005 *Phys. Rev.* B **72** 115319

[26] Brizard C, Rolland G and Laugier F 1993 *Journal of Applied Crystallography* **26** 570

[27] Ferrari A C, Meyer J C, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K S, Roth S and Geim A K 2006 *Phys. Rev. Lett.* **97** 187401

[28] Nienhaus H, Kampen T U and Monch W 1995 *Surface Science* **324** L328

[29] Barros E B, Demir N S, Souza Filho A G, Mendes Filho J, Jorio A, Dresselhaus G and Dresselhaus M S 2005 *Phys. Rev.* B **71** 165422

[30] Malarda L M, Pimentaa M A, Dresselhaus G and Dresselhaus M S 2009 *Phys. Rep.* **473** 51

[31] Ni Z H, Chen W, Fan X F, Kuo J L, Yu T, Wee A T S and Shen Z X 2008 *Phys. Rev.* B **77** 115416

[32] Röhrl J, Hundhausen M, Emtsev K V, Seyller Th, Graupner R and Ley L 2008 *Appl. Phys. Lett.* **92** 01918

[33] Emtsev K V, Speck F, Seyller Th and Ley L 2008 *Phys. Rev.* B **77** 155303

[34] Gupta A, Chen G, Joshi P, Tadigadapa S and Eklund P C 2006 *Nano. Lett.* **6** 2667

[35] Rosenberg R A, Love P G and Rehn V 1986 *Phys. Rev.* B **33** 4034