Temperature dependence of the thickness and morphology of epitaxial graphene grown on SiC (0001) wafers*

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Epitaxial graphene is synthesized by silicon sublimation from the Si-terminated 6H–SiC substrate. The effects of graphitization temperature on the thickness and surface morphology of epitaxial graphene are investigated. X-ray photoelectron spectroscopy spectra and atomic force microscopy images reveal that the epitaxial graphene thickness increases and the epitaxial graphene roughness decreases with the increase in graphitization temperature. This means that the thickness and roughness of epitaxial graphene films can be modulated by varying the graphitization temperature. In addition, the electrical properties of epitaxial graphene film are also investigated by Hall effect measurement.

Keywords: epitaxial graphene, thickness, morphology, graphitization temperature

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1. Introduction

Graphene, a single sheet of graphite, displays exciting properties which offer the possibility to replace silicon when microelectronics evolves to nanoelectronics.[1−8] However, the challenge encountered by all researchers is the preparation of uniform and high-quality graphene crystal. The method of exfoliating graphene from graphite, and the chemical vapour deposition growth of graphene on Ni or Cu films, are unsuitable for microelectronics industrial applications.[9−13] Thus far, for microelectronics industrial purposes, the best way is the high temperature sublimation of a few atomic layers of Si from a mono crystalline SiC substrate.[14] Although there are many reports about epitaxial graphene (EG) grown on the Si-face of SiC, the graphitization temperature influence has not been comprehensively investigated so far.[15−18] In the present paper, we prepare the EG at various graphitization temperatures, and investigate the effect of temperature on the thickness and the surface morphology of EG by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The results reveal that the EG thickness increases and the EG roughness decreases with the increase in graphitization temperature. In addition, the electrical properties of the EG film are also analysed by Hall effect measurement.

2. Experimental details

The 6H–SiC (0001) substrates were chemically cleaned *ex-situ*[19] prior to being loaded into the induction vacuum furnace. Once the substrates were loaded and adequate chamber vacuum was achieved ($< 3.0 \times 10^{-5}$ Pa), processing was started by hydrogen etching the surface, and the step was performed for 15 min at a pressure of 0.8 atmospheric pressure (atm, 1 atm = 1.01325×10^5 Pa) and a temperature

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of 1550 °C to remove the scratches on the top surface.

After the hydrogen etching procedure, the temperature naturally reduced down to room temperature with the protection of hydrogen at 0.8 atm, and then the hydrogen was excluded. In order to release residual hydrogen, the graphite boat was first heated to 800 °C, while the system was pumped down to 3.0×10^{-5} Pa by a turbo pump, and then argon flow was introduced into the chamber at a rate of 100 sccm. After that, the SiC substrates were gradually heated up to a temperature between 1500 °C and 1600 °C, and maintained at this temperature for a duration between 15 min and 50 min for graphitization. After the graphitization process was completed, the SiC substrates were cooled under the protection of argon for several hours.

After growth, the substrates were taken out from the chamber and then the surface morphology and thickness of the graphene films were characterized by tapping mode atomic force microscopy (AFM: SPA-300HV SPM UNIT) and X-ray photoelectron spectroscopy (XPS: Thermo ESCALAB 250), respectively. In addition, the carrier concentration and Hall effect mobility were also measured at 5 K.

3. Results and discussion

Figures 1(a) and 1(b) show AFM images of the Si-terminated 6H–SiC (0001) substrate before and after the etching hydrogen treatment, respectively. From Fig. 1(a), one can see many scratches on the surface of a cleaned SiC substrate. The scratches, as deep as several to ten nm, are distributed randomly on the surface. The root-mean-square (RMS) roughness value of the cleaned SiC substrate is 4.23 nm. Figure 1(b) shows the atomically flat terraces about 600 nm–800 nm wide after these scratches have been removed by hydrogen etching; the height profile image

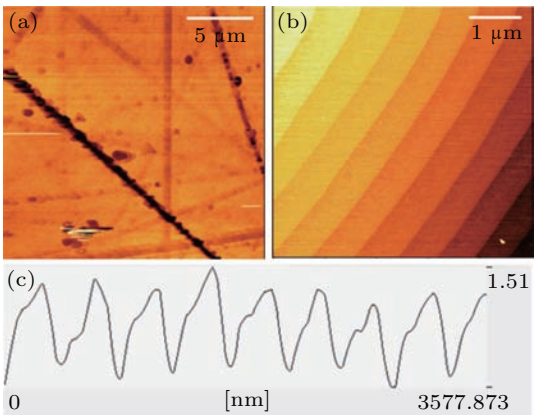


Fig. 1. (colour online) AFM images of the 6H–SiC (0001) substrate before (a) and after (b) H_2 etching, and (c) the height profiles of the terraces shown in panel (b).

(Fig. 1(c)) reveals the height between the adjacent terraces ranging from 0.6 nm to 0.8 nm, corresponding to the half unit cell height (1.5 nm) of 6H–SiC. The uniform step height along the terraces indicates identical stacking sequences of Si–C bilayers on the terraces,[20] which is very good and very similar to those reported by Emtsev *et al.*[21] The RMS roughness value is dropped down to 0.491 nm. Thus hydrogen etching provides an intrinsic surface morphology of 6H–SiC for the following graphitization.

To investigate how the graphitization temperature influences the thickness of EG, we identify the EG layers using the XPS technique,[22] which is based on a traditional overlayer-substrate attenuation model.[23] Figure 2(a) shows the XPS spectra taken on the samples with varying graphitization temperatures from 1500 °C to 1600 °C. From the C1s XPS spectrum at 1500 °C, the EG peak is not observed; however, the peak of the $6\sqrt{3}$-reconstructed layer is found, which reveals strong surface carbon enrichment.[24] The EG peak (284.7 eV) is detected when the graphitization temperature is higher than 1550 °C. It is noted that the intensity ratio between the EG peak and SiC peak (283.7 eV) increases with increasing temperature, which corresponds to the increase in EG thickness. As displayed in Fig. 2(b), the thickness of EG increases from 1.23 to 2.84 layers, while the graphitization temperature varies from 1550 °C to 1600 °C. So we can conclude that the thickness of EG can be modulated by varying the graphitization temperature. Furthermore, we also study the effect of graphitization time on the thickness of the EG film. Figure 2(c) shows the XPS spectra taken on the samples with varying graphitization time at 1550 °C. The result reveals that the thickness increases from 1.23 to 1.54 layers, while the graphitization time varies from 15 min to 50 min, as shown in Fig. 2(d).

In order to further investigate the influence of graphitization temperature on the surface morphology of EG films, the samples were characterized by AFM. Figures 3(a)–3(c) reveal the AFM images of EG films prepared at different graphitization temperatures. Their morphologies are similar to those reported in Refs. [21] and [25]. As shown in Fig. 3(d), the EG roughness decreases with the increase in graphitization temperature. When the graphitization temperature reaches 1600 °C, the RMS roughness value is 0.41, which is slightly less than the RMS roughness value of etched SiC substrate. The decrease in EG roughness can be attributed to the EG thickness increasing with increasing temperature, which is consistent with the XPS results shown in Fig. 2(a).

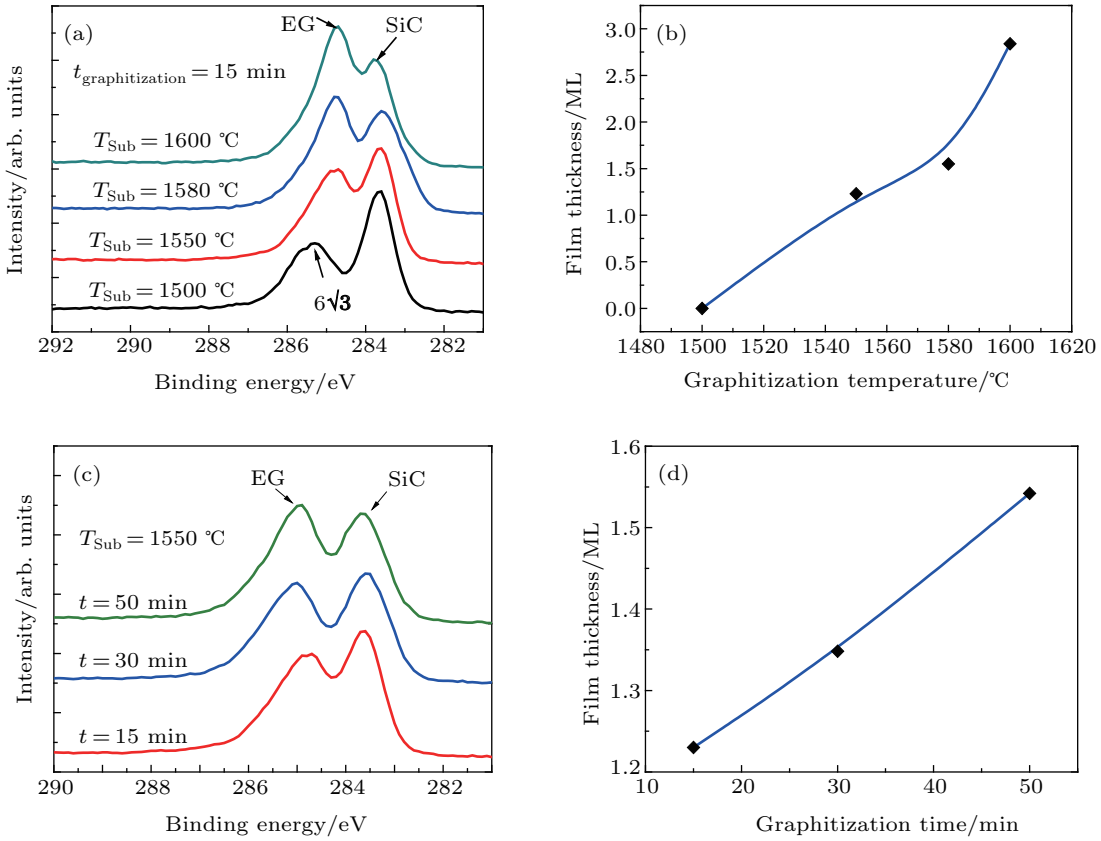


Fig. 2. (colour online) (a) XPS-C1s spectra taken on graphitized 6H–SiC (0001) substrates under various graphitization temperatures; (b) the evolution of thickness with graphitization temperature; (c) XPS-C1s spectra taken on graphitized 6H–SiC (0001) substrates at 1550 °C for various graphitization times; (d) the evolution of thickness with graphitization time.

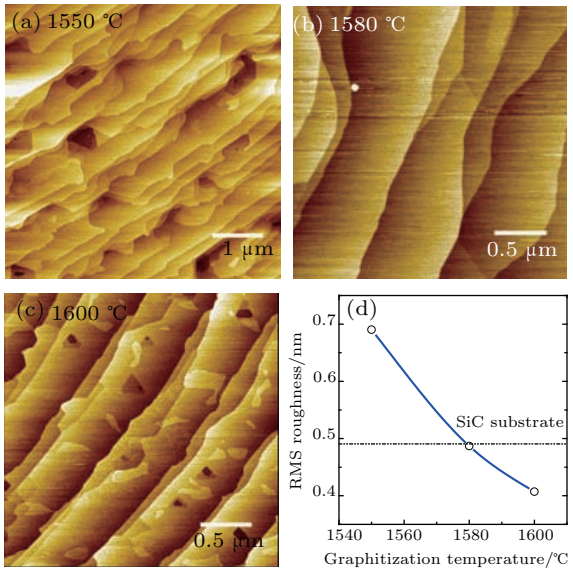


Fig. 3. (colour online) (a)–(c) The surface morphology change with temperature on the Si face 6H–SiC (0001) wafer; (d) the RMS roughness of the graphene films versus graphitization temperature. The horizontal dashed line represents the RMS roughness of the SiC substrate.

In addition, we also study the electrical properties of EG film grown at 1550 °C for 15 min by Hall effect measurement. The typical size of the van der Pauw configuration is 5 mm × 5 mm. Figure 4 shows the plot of Hall resistance (R_{XY}) versus magnetic flux density ($\mu_0 H$), recorded at 5 K. The carrier mobility and concentration can be approximated, respectively, by

$$\mu = \frac{S}{R_s} \tag{1}$$

and

$$n_s = \frac{1}{qS}, \tag{2}$$

where $S = 13.87$, which shows that the slope can be linearly fitted from Fig. 4, and q is the electronic charge ($q = 1.6 \times 10^{-19}$ C). The measured sheet resistance R_S is 251 Ω/□. Therefore the electron mobility and concentration are calculated to be $\mu = 553$ cm^2/V·s and $n_s = 4.5 \times 10^{13}$ cm^{-2}, respectively. The electron mobility is lower and the electron concentration is higher than their counterparts given in Ref. [21]. The present semi-insulating SiC substrate is not intrinsic semi-insulating but obtained by Vanadium doping, which might cause the degradation in the electrical properties of the graphene layer.

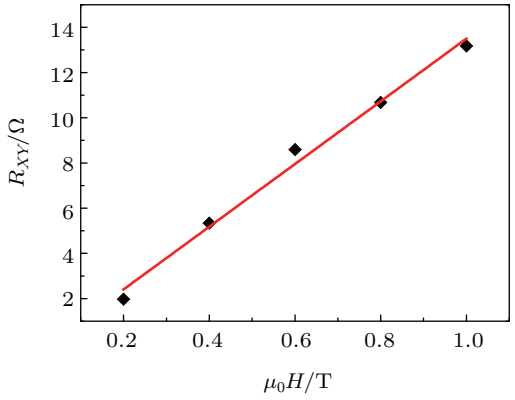


Fig. 4. (colour online) Evolution of the magnetic flux density ($\mu_0 H$) with Hall resistance (R_{XY}).

4. Conclusions

EG films are successfully grown on an 6H–SiC (0001) substrate. The XPS results reveal that the EG films begin to form when the temperature exceeds 1550 °C, and the EG thickness increases with the elevation of graphitization temperature. From the XPS spectra, we also observe the increase in EG thickness with the increase in graphitization time. The AFM images demonstrate that the EG roughness decreases with the increase in graphitization temperature, which corresponds to the increase in thickness. In addition, the electrical properties of the EG film are analysed by Hall effect measurement. The results reveal that our EG film has a Hall mobility of 553 $cm^2/V{\cdot}s$ and an electron concentration of 4.5×10^{13} cm^{-2} at 5 K, respectively.

References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 *Nature* **438** 197

[2] Zhang Y, Tan Y W, Stormer H L and Kim P 2005 *Nature* **438** 201

[3] Berger C, Song Z, Li X, Wu X, Brown N, Naud C, Mayou D, Li T, Hass J, Marchenkov A N, Conrad E H, First P N and de Heer W A 2006 *Science* **312** 1191

[4] Bostwick A, Ohta T, Seyller Th, Horn K and Rotenberg E 2007 *Nat. Phys.* **3** 36

[5] Zhou B H, Duan Z G and Zhou B L 2010 *Chin. Phys.* B **19** 037204

[6] Brihuega I, Mallet P, Bena C, Bose S, Michaelis C, Vitali L, Varchon F, Magaud L, Kern K and Veuillen J Y 2008 *Phys. Rev. Lett.* **101** 206802

[7] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 *Rev. Mod. Phys.* **81** 109

[8] Fu Z G, Wang Z G and Li S S 2011 *Chin. Phys.* B **20** 058103

[9] 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

[10] Yu Q K, Lian J, Siriponglert S, Li H, Chen Y P and Pei S S 2008 *Appl. Phys. Lett.* **93** 113103

[11] Reina A, Jia X T, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2009 *Nano Lett.* **9** 30

[12] Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J H, Kim P, Choi J Y and Hong B H 2009 *Nature* **457** 706

[13] Li X S, Cai W W, An J H, Kim S Y, Nah J, Yang D X, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee S K, Colombo L and Ruoff R S 2009 *Science* **324** 1312

[14] Berger C, Song Z M, Li T B, Li X B, Ogbazghi A Y, Feng R, Dai Z T, Marchenkov A N, Conrad E H, First P N and de Heer W A 2004 *J. Phys. Chem.* B **108** 19912

[15] Sadowski M L, Martinez G, Potemski M, Berger C and de Heer W A 2006 *Phys. Rev. Lett.* **97** 266405

[16] Wu X, Li X, Song Z, Berger C and de Heer W A 2007 *Phys. Rev. Lett.* **98** 136801

[17] de Heer W A, Berger C, Wu X, First P N, Conrad E H, Li X, Li T, Sprinkle M, Hass J, Sadowski M L, Potemski M and Martinez G 2007 *Solid State Commun.* **143** 92

[18] Wang D C, Zhang Y M, Zhang Y M, Lei T M, Guo H, Wang Y H, Tang X Y and Wang H 2011 *Acta Phys. Sin.* **60** 128101 (in Chinese)

[19] Lew K K, VanMil B L, Myers-Ward R L, Holm R T, Charles R, Eddy Jr and Gaskill D K 2007 *Mater. Sci. Forum* **513** 556

[20] Li X B 2008 *Epitaxial Graphene Films on SiC: Growth, Characterization, and Revices* Ph. D. Thesis (Atlanta: Georgia Institute of Technology)

[21] Emtsev K V, Bostwick A, Horn K, Jobst J, Kellogg G L, Ley L, McChesney J L, Ohta T, Reshanov S A, Röhrl J, Rotenberg E, Schmid A K, Waldmann D, Weber H B and Seyller T 2009 *Nat. Mater.* **8** 203–207

[22] Emtsev K V 2009 *Electronic and Structural Characterizations of Unreconstructed SiC* {0001} *Surfaces and the Growth of Graphene Overlayers* Ph. D. Thesis (Erlangen: der Universität Erlangen-Nürnberg)

[23] Briggs D and Seah M P 1994 *Practical Surface Analysis: Auger and X-Ray Photoelectron Spectroscopy* (Singapore: John Wiley & Sons Ltd)

[24] Varchon F, Feng R, Hass J, Li X, Ngoc Nguyen Naud B C, Mallet P, Veuillen J Y, Berger C and Conrad E H 2007 *Phys. Rev. Lett.* **99** 126805

[25] Borovikov V and Zangwill A 2009 *Phys. Rev.* B **80** 121406